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Hollow Cathode Discharges

Analytical Applications

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The low pressure glow discharges considered in this paper are the hollow cathode (Paschen), and the flat cathode (Grimm). Both discharges have similar voltage—current characteristics which are responsible for their radiation stability. The analytical sample is supplied to the discharge through a sputtering mechanism which provides a stable and non-selective source of particles. Some of the fundamental properties of the glow discharge and sputtering phenomena will be discussed, including the relation between the geometry of the discharge, and the nature and pressure of sustaining gas, and current, on the emission characteristics of the discharges. These will be followed by a description of the conventional instrumentation developed for analytical purposes using the hollow cathode and flat discharge. A description of the hollow cathode developed at the National Bureau of Standards (NBS) will follow. The techniques used for the introduction of various conductive and non-conductive materials into the discharge will be discussed. The use of these discharges will be illustrated with examples taken from the literature and from the measurements performed at NBS. The paper will conclude with a discussion of possible future developments of low pressure glow discharges. A collection of references to works on low pressure glow discharges, containing 690 entries, concludes this work.

Key words: Grimm discharge; hollow cathode discharge; low pressure glow discharges; Paschen discharge; planar cathode discharge; pulsed discharge.

1. Introduction

The energy necessary to excite the radiations from various free particles—atoms, ions, molecules, and free radicals—originating from the analytical sample, and required in analytical emission spectroscopy, can be supplied in a variety of forms according to the excitation source used. Table 1 enumerates these sources which are divided in a somewhat arbitrary manner into two general categories: electrical discharges and thermal sources.

The production of free particles and their excitation through the use of high temperature furnaces or combustion flames is a purely thermal phenomenon. When electrical discharges are used for the same purpose, the production of free particles and their excitation often result from a combined effect of the energy developed in the electric field and thermal energy. An extreme case in this regard is illustrated by the dc arc where the thermal energy is the determining parameter. The other extreme, where the production of free particles and their excitation results from the energy generated in electric fields, is illustrated by the low pressure glow discharges, namely the planar and hollow cathode discharge. Although in this case a certain amount of heat is generated as a result of ion bombardment at the cathode, this thermal energy is only incidental to the process and is not necessary for the production and maintenance of the discharge, for the generation of free particles, and for the subsequent excitation processes which occur in these sources.

The basic conditions required from an excitation source are: capability to be supplied in a controlled

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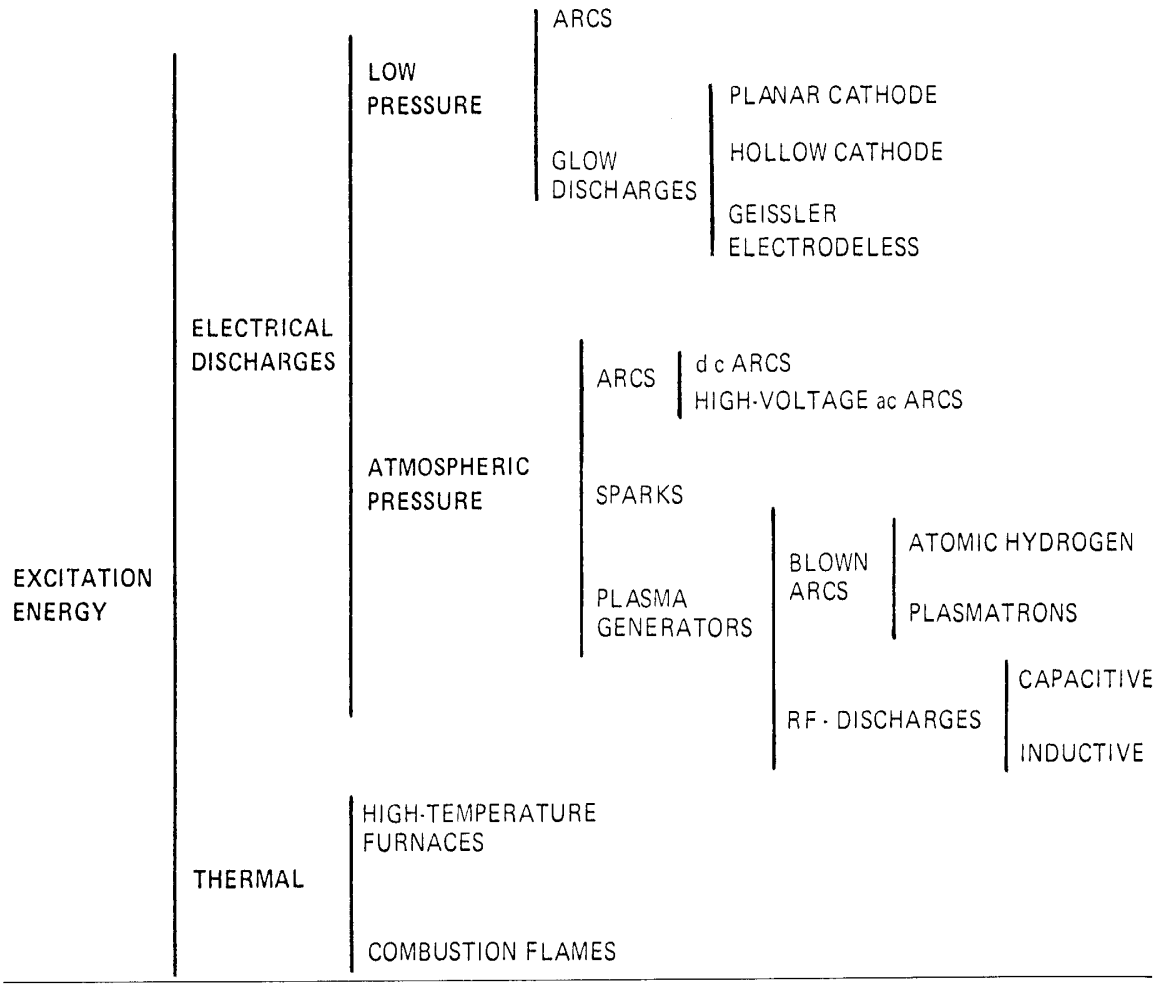
Table 1. Sources of energy used in analytical emission spectroscopy to excite the radiations from atoms, ions, molecules, and free radicals.



manner with the analytical sample in solid, liquid, or gaseous state for both electrically conductive and non-conductive materials. The excitation source should excite all the chemical species of interest with high sensitivity and stability. Furthermore, interferences due to matrix effects, interelement actions, chemical reactions, and selective energy transfers should be as small as possible. These interferences are associated to a large extent with those excitation sources in which the production and excitation of particles result from thermal energy, where the thermal characteristics of each chemical species such as melting, boiling, and vaporization temperatures, vapor pressure, dissociation, are specific for every chemical species and play a determining role. Self-absorption is also a phenomenon often associated with thermal excitation and is responsible for loss of sensitivity and non-linearity between the emission intensity and actual sample concentration. The processes occurring in the excitation source become even more complex when the energy generated by an electrical field is associated with the thermal energy. From the various sources of excitation mentioned in table 1, the electrical glow discharges produced under low pressure, and in particular the planar cathode and hollow cathode discharges mentioned previously, are less subjected to the processes discussed in the foregoing, and are also practically free of self-absorption.

The sputtering phenomenon, responsible in this case for the production of free particles from the analytical sample, is less subjected to selectivity, and the absence of oxygen from the gas supporting the discharge eliminates the matrix and chemical reactions interferences resulting from the action of oxygen on the sample.

Based on these considerations we have initiated a study of the low pressure glow discharges and some of the results obtained in our preliminary experiments will be discussed in this work together with factual data from the available scientific literature.

2. Production and General Characteristics of Low Pressure Glow Discharges[1]

Low pressure glow discharges of the type pertinent to our interests here can be produced using a simple cylindrical glass tube provided with two electrodes of adequate shape, an inlet for the gas sustaining the discharge, and a vacuum connection, as illustrated after Francis [105] in figure 1. The tube is filled with a rare gas, say

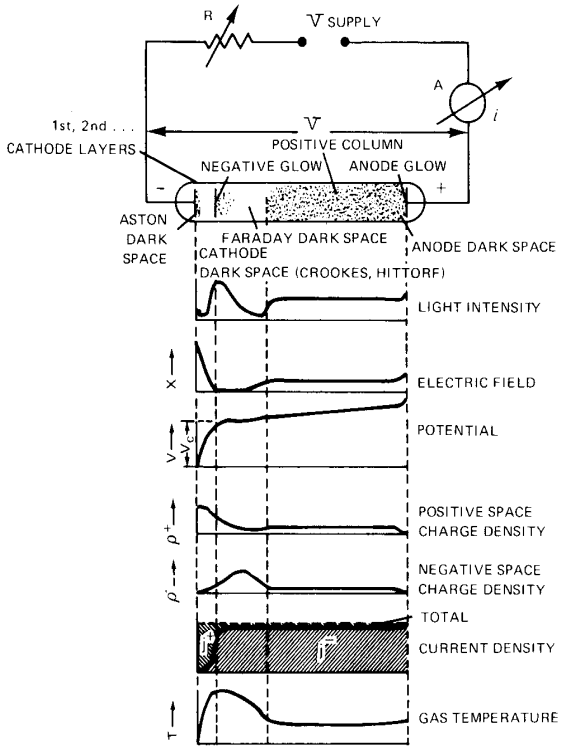


Figure 1—Characteristics of a low pressure glow discharge. After Francis [105].

helium or argon, at a pressure between 1 to 20 Torr, and a dc potential V is applied across the electrodes, through a current limiting resistor R. If the dc potential V, is increased by changing the value of the variable resistance R, a small current i is detected by the sensitive meter A. An intermittent discharge, produced in random bursts, is thus observed at very low values of i of the order of 10^{-18} A. As the potential V is further increased, the current i increases rapidly and rises to values exceeding those determined by the resistance R. Under these conditions a dark self-sustained discharge is produced and the voltage at which this phenomenon is observed is called the breakdown voltage V_b (of the order of 1000 V). Such discharges are called dark discharges or Townsend discharges, and are characterized by currents of the order of 10^{-6} A under practically constant voltage. This is illustrated in figure 2 by the region AB [257]. As the current is further increased, the voltage decreases through a transitional region CD (subnormal glow discharge), and reaches a constant value V_n at the point D. A visible glow discharge is now produced at the normal cathode fall potential V_n (of the order of 200 to 300 V). This potential remains practically constant for large variations of the current from about 10^{-4} A to about 0.1 A.

With a further increase of the current the limited cathode area becomes current saturated, whereupon the voltage rises and the discharge enters in the abnormal mode of operation described by portion EF of the curve on figure 2. If the current is increased again, the voltage goes first through a sharp increase followed at F by a transition region and a sudden drop, reaching values of the order of several tens of volts for currents of the order of 10 A; this is the arc discharge. A significant characteristic of this type of discharge is heating of the sustaining gas.

The glow discharge defined by the points D-E-F on figure 2 is of interest to the analytical spectroscopist and

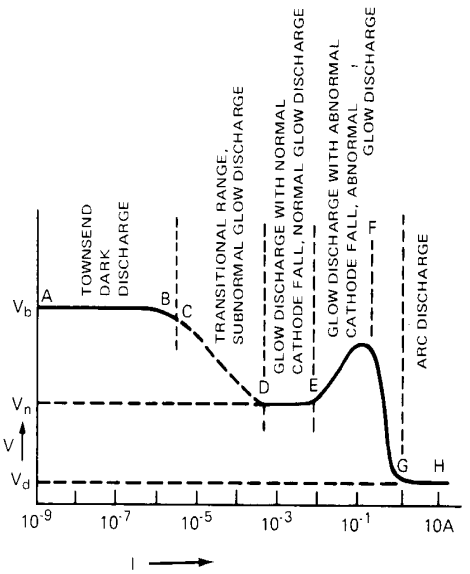


Figure 2—Voltage-current characteristics of a self-sustained low pressure glow discharge. After Penning [257].

[1]Most of the information presented in this section is based on the fundamental works of G. Francis [105] and F. M. Penning [257], the bracketed figures indicating references appearing at the end of this paper. Information was also obtained from other sources [94, 213, 252, 257, 365, 386 and *10*].

NOTE: Bracketed numerals in roman type identify the 400 citations assembled in the main body of Section 5, Collection of References to Works on Low Pressure Glow Discharges. Bracketed numerals in italic type identify papers in a 290-citation addendum to this collection, also part of Section 5.

can be produced directly by raising the potential V to the value V_n. The appearance of this discharge varies, for the same gas, with the geometry of the electrodes and that of the discharge tube, the distance between the electrodes, the pressure of the sustaining gas, the current, and the nature of the electrodes. These parameters were selected here to produce a discharge which is closely related in its properties to the discharge used in analytical applications.

2.1 Characteristics of the Low Pressure Glow Discharge

The glow discharge described schematically in figure 1 consists of a number of alternating dark and luminous zones. Their existence, disposition, and size depend on the experimental conditions; however, the example chosen here describes the general case of a discharge obtained in a glass tube 30 cm long and 5 cm wide, provided with flat copper electrodes having a diameter of 2.5 cm placed inside the tube 15 cm apart. The gas is helium at a pressure of 10 Torr and the current is 50 to 100 mA. Under these conditions the following zones are observed: at the cathode there is a very thin dark layer called the Aston primary or dark space. This is followed by a weakly luminous cathode layer, and a second dark zone called the Crookes or Hittorf dark space. Following this dark space, and sharply defined toward the cathode, is the strongly luminous negative or cathode glow. The luminous intensity of the cathode glow decreases toward the anode as it merges into another dark space called the Faraday dark space. Between this dark space and the anode there is another luminous zone, called the positive column, separated from the anode by another thin dark space and an anode glow at the surface of the electrode. The variation of the light intensity, electric field, potential, positive space charge density, negative charge density, current density, and gas temperature are described qualitatively in figure 1 [105].

An increase of pressure results in a compression of the cathode dark space, negative glow and Faraday dark space which contract toward the cathode. A decrease of pressure produces a reverse effect, and, if the voltage is not increased, the discharge goes out. A decrease of the distance between the cathode and anode produces a shortening of the anode glow, which disappears altogether where the anode is in the proximity of the cathode. When the anode is near the cathode edge of the negative glow, the voltage necessary to sustain the discharge rises rapidly and the discharge is said to be obstructed. This proves that the positive column is not essential for maintaining the low pressure glow discharge, while the part of the discharge at the cathode, including the Aston and Crookes dark spaces, are indispensable. An increase in voltage results in an increase in the radiation intensity of the discharge, in particular at the cathode, and the definition of the various zones becomes sharper [105].

Unlike the conductivity of electricity in solids, the elementary processes occurring when an electrical current passes through a gas are numerous and complex. They have been summarized by Penning in the diagram from figure 3 [257]. From these, the excitation and ionization processes are the most significant in relation to the subject discussed here.

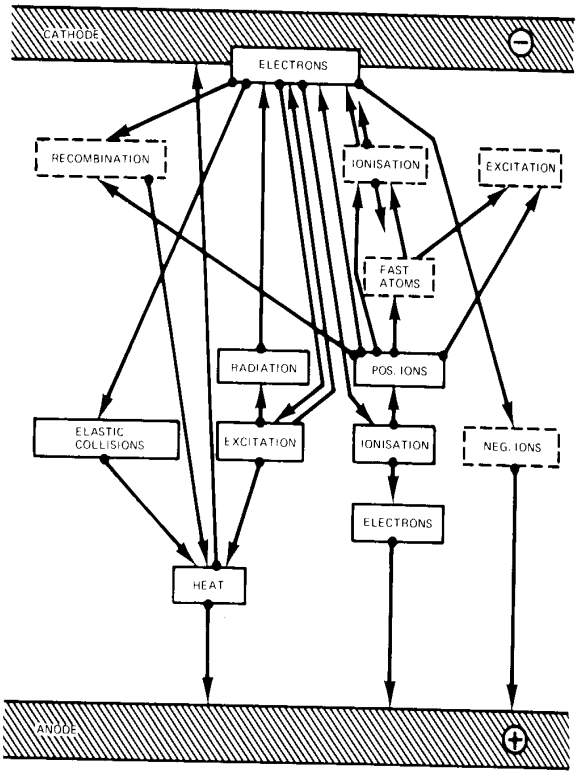


Figure 3—Diagrammatic summary of several elementary processes occurring in a low pressure glow discharge. Each process originates at the dot and ends at the arrowhead. After Penning [257]. [Courtesy of Philips Technical Library and Servire BU; Katwijk aan Zee, Netherlands, Publisher.]

The Aston dark space is characterized by the presence of electrons of low energy originating from the cathode. In the first thin layer of the negative glow these electrons are accelerated sufficiently to excite the particles found in this zone. They lose this energy in the Crookes or Hittorf dark zone. The excitation occurring in the strongly luminous negative glow is produced by the numerous electrons resulting from the ionization process occurring in the cathode dark space as well as by the few faster ones originating from the cathode. Positive ions are also generated in this zone and are attracted toward the cathode. As a result of their impact

on the cathode, atoms from this cathode are ejected and reach the glow discharge zone producing a sputtering of the material from which the cathode is made. Under these conditions a mixture of atoms from the supporting gas and from the material from the cathode are always present in the negative glow zone where they are strongly excited by collision with the ions and electrons present there [105].

The Faraday dark space is characterized by the presence of ground-state particles and low energy electrons which have lost this energy in the negative glow zone. After these electrons gain once more sufficient energy, from the electric field which accelerates them toward the anode, they produce the luminous positive zone. A spectroscopic examination of the radiations excited in this zone reveals the presence of the atomic spectra from helium which is the sustaining gas used in this example.

The same examination of the negative glow discharge reveals that, in addition to the radiations from the sustaining gas, strong emissions from the sputtered particles from the cathode are excited and emit radiations from neutral atoms, ions, and molecules. It is this basic property, i.e., the generation of free particles through sputtering and their subsequent excitation by non-thermal processes in the negative glow region, that makes the low pressure glow discharge a valuable source in analytical spectroscopy.

Further information concerning various characteristics of low pressure glow discharges will be found in references *10*, *177*, *180*, *226*, and *252*.

3. The Low Pressure Glow Discharge as an Excitation Source in Emission Spectroscopy

3.1 The Planar Discharge

Described diagramatically in figure 1, the actual aspect of this simplest form of low pressure glow discharge is illustrated in figure 4 which was obtained under the conditions described previously. The copper cathode is at left, the copper anode at right, and the principal zones seen are the strongly luminous negative glow at the cathode, followed by the Faraday dark space, the positive column, and the anode glow. The thin Aston and Crookes dark spaces, and the faint cathode layer and the anode dark space cannot be distinguished on this photograph.

As discussed previously, the zone of interest is the negative glow since the particles sputtered from the cathode, which in this case is the analytical sample, are strongly excited in this zone and produce the spectra of the neutral and ionized atoms together with pertinent

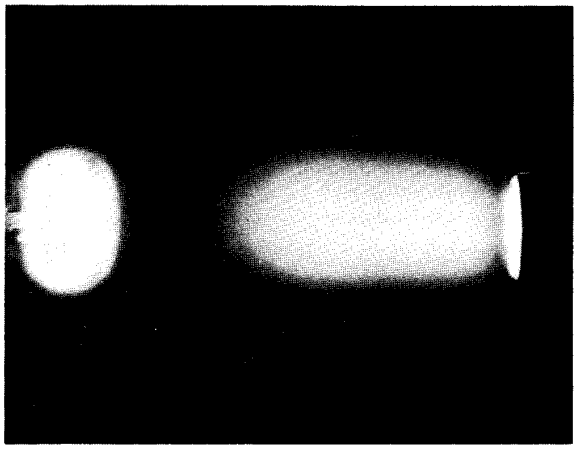


Figure 4—A low pressure glow discharge produced between two copper disc electrodes in helium at 10 Torr and 100 mA. The cathode is at left, the anode at right.

molecular spectra. The positive column and the anode glow, which are not needed to produce or maintain the discharge, can be eliminated altogether by bringing the anode electrode near the cathode, and by placing this anode outside the field of examination of the cathode glow. It is from this basic and simplest form of the flat or planar glow discharge that Grimm has developed a discharge tube that is now used routinely as an excitation source in analytical emission spectroscopy [128, 129]; a diagrammatic description of this discharge tube is given in figure 5. It consists of a cylindrical anode and cathode unit, made usually of a copper alloy, and separated by an insulator. The distance between the cathode and the anode is about 0.2 mm. The metallic analytical sample, in the shape of a flat disc, is placed against the cathode provided with a vacuum tight "O" ring, and is in electrical contact with the cathode. The anode is closed with a vacuum tight window. An adequate gas, usually

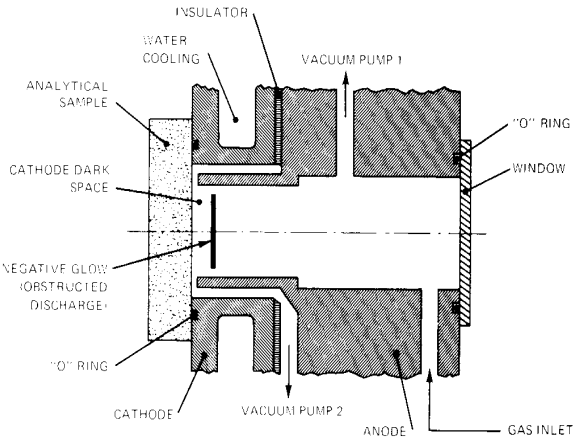


Figure 5—Diagrammatic description of the planar low pressure glow discharge developed by Grimm [128, 129].

argon or helium, is introduced in the lamp at a pressure of 1 to 20 Torr and flows continuously through the unit. The cathode body is water cooled.

Under these conditions, when a dc current of 100 to 600 mA and 700 to 2500 V is supplied to the lamp, a glow discharge is produced in front of the cathode, inside the anode space. This discharge is the negative glow described previously in figures 1 and 4. It has the characteristics of an obstructed discharge, and, is suspended free of any material contacts with the two electrodes, being isolated from the walls of the anode by a circular gap, which in fact is the anode dark space, and separated from the cathode by the cathode dark space. The intensely luminous negative glow has a thickness of the order of the mean free pathlength of the particles, and consists mostly of excited particles sputtered continuously and uniformly from the analytical sample and from the supporting gas. The dc current can be supplied to the discharge in an uninterrupted manner or in a pulsed mode. The pulsed mode is generally used with analytical sample subjected to overheating when undergoing the sputtering process.

The glow discharge source developed by Grimm can be obtained from RSV-Präzisionmessgeräte, GmbH Hauptstrasse 60, D-8031 Seefeld 2, West Germany,[2] including the source, the vacuum system, and the dc power supply for continuous or pulsed operation. The RSV company is represented in North America by Labserco Ltd. Unit 8 1100 Invicta Drive, Oakville, Ontario L6H 3K9. A similar low pressure glow discharge source using a planar cathode is manufactured in this country under the name "Cathaquant" by the Spectrogram Corp., 385 State Street, North Haven, CT 06473. A detailed study of the functioning characteristics of this discharge source was made by Grimm [128, 129], Boumans [40], and by Dogan, Laqua, and Massmann [85, 86] and El Alfy, Laqua, and Massmann [93] at the Institut für Spektrochemie und Angewandte Spektroskopie in Dortmund, Germany, and all the data used, and the statements made in the following discussion, are taken from these basic contributions. Further contributions were made by Boumans [41].

The current-voltage characteristic of the discharge is illustrated in figure 6(a) for various pressures, using argon as the carrier gas and nickel for the cathode. This parameter depends, for a given current, also on the type of carrier gas and its pressure and on the type of cathode sample material. The relative intensity of the Ni 3610.46 Å line as a function of the current supplied to the lamp and for several argon pressures also is given in figure 6(b). These measurements were made with a 1.5 m direct reading grating spectrometer [129].

The linear relation between the concentration of a chemical element and the corresponding signal intensity obtained with the Grimm glow discharge source is illustrated in figure 7 for Sb in Cu-Pb-Sn(a), Cu in Al(b), Zn in Al(c), and Mn in Al(d) matrices, in comparison with a conventional spark.

The matrix effect is illustrated in (c) and (d) of figure 7 for Zn and Mn in Al and in AlMg and AlMgSi alloys,

[2]In order to adequately describe materials and experimental procedures, it is occasionally necessary to identify a commercial product by a manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

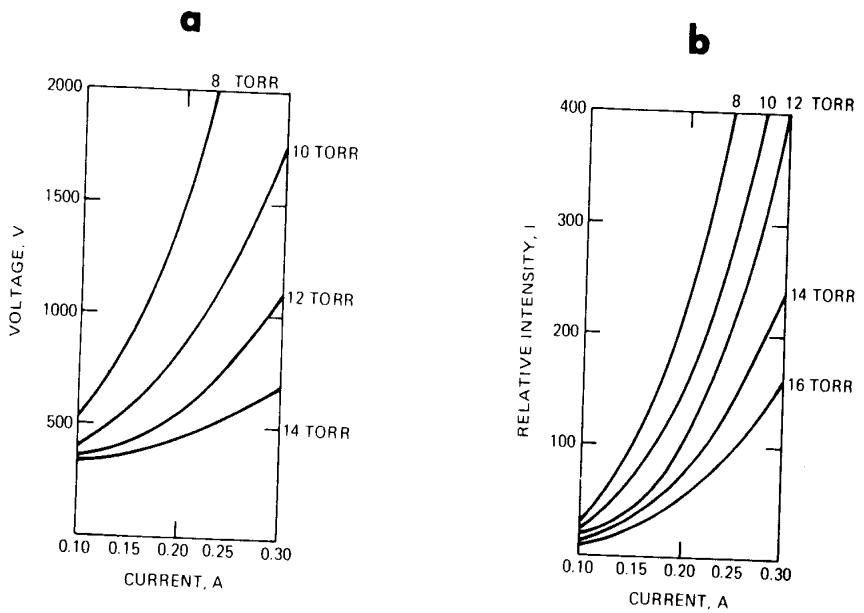


Figure 6—Voltage-current characteristics of the discharge from figure 5, in argon (a), and (b), the relative intensity of the Ni radiation at λ 3610.46Å as a function of the current supplied to the discharge in argon [129].

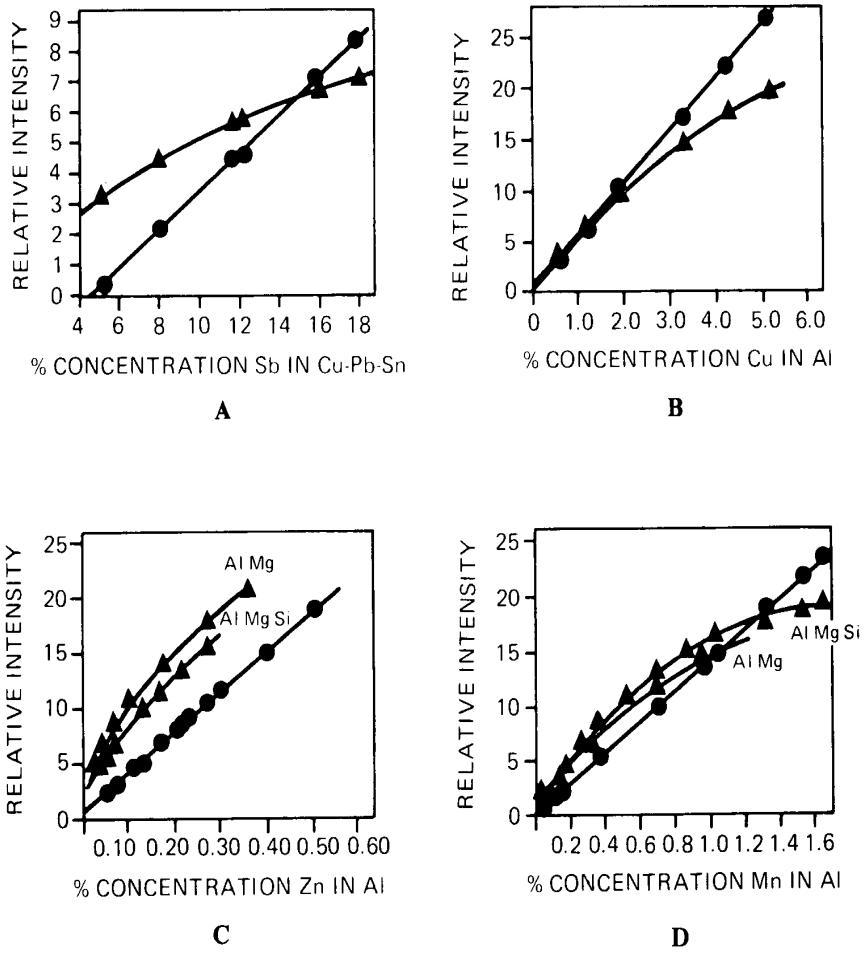


Figure 7—Relation between the concentration of a chemical element and the corresponding signal intensity obtained in a Grimm glow discharge source in comparison with a spark source for: Sb in Cu-Pb-Sn (A); Cu in Al (B); Zn in Al, Al-Mg, and Al-Mg-Si (C); and Mn in Al; Al-Mg, and Al-Mg-Si (D) samples. After Grimm.

determined with the glow discharge source and a conventional spark source. In all cases the glow discharge was operated in argon at a pressure of 5 to 7 Torrs and a discharge current of 0.15 to 0.25 A. A preburn of 10 to 40 s and an integration time of 3 to 40 s were used for the glow discharge.

The detection sensitivity of the planar glow discharge was determined for several elements by Grimm [129] and is given in table 2.

Table 2. Detection sensitivity for the glow discharge source after Grimm [129]

Element	Line Å	Detection limit (ppm)
Beryllium	2494.73	2
Silicon	2881.58	5
Iron	3020.64	80
Magnesium	2795.53	80
Chromium	4254.35	20
Molybdenum	3864.11	10
Aluminum	3961.52	100
Lead	4057.83	100

This detection sensitivity can be increased by looking at the negative glow sidewise [85], or by using the glow-discharge in the hollow cathode mode; this mode of operation will be discussed later in this work.

Further physical characteristics of the glow discharge source were investigated by Dogan, Laqua, and Massmann [85], using a lamp similar to that developed by Grimm, but with additional water cooling of the analytical sample. This provision permits the use of higher currents without overheating the sample.

When a new sample with a fresh surface is submitted to the discharge, the current exhibits a certain instability. This is due to surface impurities and oxides. After the surface has been cleaned through the sputtering process, the discharge stabilizes and "burns" quietly. Aluminum surfaces require a longer cleaning time (40s) while zinc cleans after a shorter preburn (3s) both in argon. The preburn time depends also on the carrier gas and is shorter in krypton than in argon or neon.

The analytical sample is supplied to the discharge as an electrical conducting flat disc with a smooth surface. It is pressed against the cathode which is provided with

an "O" ring to insure a vacuum tight seal. The surface sample exposed to the discharge is 0.28 cm^2. It is desirable that this surface be representative of the sample, homogeneous, and with particles having a diameter less than 0.1 mm for electrically conducting samples. Non-conducting samples can be mixed with a conducting powder material such as copper, silver, or graphite and pressed to produce the disc-shaped sample.

The amount of material sputtered during the discharge, for the same discharge conditions, i.e., current, gas, pressure, exposed surface, time, depends on the sample material. For instance, the amount of material sputtered in one minute is 0.34 mg for aluminum, 1.0 mg for copper, 3.1 mg for zinc, and smaller amounts for graphite and carbon. When arranged in increasing order, carbon sputters least and is followed by aluminum, iron, steel, copper, brass, and zinc. The amount of sputtered material per unit of time increases with the increase of current. For a power of 90 w the amount of aluminum sputtered is 0.30 mg/min in neon, 0.34 mg/min in argon, and 0.38 mg/min in krypton.

As already mentioned, the spectra excited in a low pressure glow discharge are characterized by the presence of radiations originating from the atoms, ions, molecules, and free radicals from the analytical sample and the carrier gas. The initial emissions originate from the impurities and oxide layers formed at the surface of the sample. After these layers are eroded through the sputtering process, the spectra observed are emitted by the elements which constitute the analytical sample, together with those from the carrier gas, and sometimes with the molecular emission from OH and N_2 as impurities. The intensities of these emissions depend on the concentration of the corresponding elements in the sample, the discharge parameters, the geometry of the discharge lamp, and on the carrier gas. In general an increase in current supplied to the discharge increases the radiation intensity. For instance, a twofold increase in current from 60 mA to 120 mA produces a fivefold increase in the intensity of magnesium emission at λ 2852.13 Å, at an optimum argon pressure of about 8 Torr.

Another property of the discharge is the continuum emission from the carrier gas. For argon this emission is stronger toward the longer wavelengths, while for krypton it is stronger for the short wavelengths.

All the parameters discussed above should be taken into consideration when the Grimm low pressure glow discharge is used for quantitative analyses since they all affect the sensitivity, precision, and accuracy of the measurements.

The essential characteristics of the low pressure glow discharge can be summarized as follows.

– The excitation conditions prevailing in the discharge produces for *all known chemical species*, radiations originating from atoms, ions, and molecules (free radicals) with *narrow natural spectral line width* and radiations which are, under the experimental conditions described in this work, practically *free of self-absorption*.

– The generation of particles and their supply into the discharge results from a *non-thermal and a practically non-selective cathode sputtering process*.

– The discharge is produced in an inert gas at low pressure and may be used directly as an excitation source in the vacuum ultraviolet.

– As a result of its *current-voltage characteristics*, the discharge is *particularly stable*.

– The discharge is silent.

The use of the Grimm discharge for the quantitative analysis of electrically conductive and non-conductive samples was studied in detail by Dogan, Laqua, and Massmann [86], and by El Alfy, Laqua and Massmann [93], and some of their results will be summarized here. The detection limits measured for several trace elements in aluminum are given in table 3 and were obtained using argon as a carrier gas at a current of 100 mA and 900 V and with a preburn of 45 s and an exposure of 6.5 min. These detection limits compare favorably with those obtained with sparks and interrupted ac arcs.

Lower detection limits were observed in krypton for atomic radiations, while neon produced lower detection limits for radiations originating from ions. With argon the detection limits were similar for both atomic and ionic radiations; therefore, this gas presents the best compromise.

Table 3. Detection limits for several elements determined with the Grimm discharge lamp [86].

Element and wavelength, Å*	Detection Limits in Percent for Medium quartz spectrograph	3.m grating spectrograph
Cu I, 3247.54	4.0×10^{-5}	1.5×10^{-6}
Fe I, 3020.64	3.0×10^{-3}	2.1×10^{-4}
Mg I, 2852.13	1.2×10^{-4}	8.5×10^{-6}
Mg II, 2795.53	1.1×10^{-4}	8.5×10^{-6}
Mn I, 2794.82	1.8×10^{-4}	1.4×10^{-5}
Mn II, 2576.10	1.1×10^{-4}	2.2×10^{-5}
Mn II, 2593.73	2.4×10^{-4}	4.6×10^{-5}
Si I, 2881.58	4.0×10^{-4}	2.7×10^{-5}
Si I, 2516.11	1.1×10^{-4}	9.4×10^{-6}
Ti I, 3653.50	1.7×10^{-3}	—
Ti II, 3349.41	3.8×10^{-3}	1.6×10^{-5}
Zn I, 3345.02	1.5×10^{-3}	3.6×10^{-5}

*As given in *Tables of Spectral-line Intensities*, W. F. Meggers, Ch. H. Corliss and B. F. Scribner. NBS Monograph 145, Part I, 1975.

The detection limits measured for the same elements in electrically non-conducting materials produced somewhat higher values. In this case the non-conductive sample was mixed with a conducting powder such as copper (reduced) silver, aluminum or graphite in a ratio of up to 1 to 1 sample to metal by volume, and the mixture was pressed (8 to 10 tons/cm^2) into a circular disc 1 to 2 mm thick.

Table 4 presents a comparison between analytical data obtained through chemical procedures (Chem.) and by emission spectrometry with the Grimm discharge source (GDS) on a variety of non-conducting sample materials [93]. These data are the average of 10 separate measurements. In this case 50 mg of the pulverized sample was mixed with 950 mg of copper powder (Merck No. 2715) and pressed into a 10 mm diameter disc at a force of at least 8 tons. The standards were obtained by mixing and diluting the oxides of Si, Al, Fe, Ti, Mg. and Mn in a Ca CO_3 matrix to produce the desired range of known concentrations. The discharge was operated in argon at a current of 160 mA, using a preburn of 60 to 180 s and an exposure time of 2 to 10 min. The spectra were recorded on photographic plates and the spectral line densities were measured with a micro-densitometer using copper as an internal standard.

These data demonstrate that the Grimm source is capable of performining spectrometric analyses with excellent precision and accuracy, and that the precision is probably related to the inevitable limitations of the photographic plate used as a receptor. Table 4 also shows that the concentration spread for the 10 elements determined extends from about 0.01 to several tens percent, covering the minor and major constituents range.

A modified Grimm discharge is described in references *4*, *37*, *43*, *44*, and *223*.

The measuring sensitivity of the low pressure planar glow discharge can be increased by producing the discharge in the hollow cathode mode.

3.2 The Hollow Cathode Discharge

3.2.1 Production of the Discharge

The aspect of a low pressure glow discharge is illustrated in its simplest form in figure 4, which was obtained with a single flat cathode. If a second flat cathode is now placed in the discharge tube and the two cathodes are separated by a gap of approximately 25 mm, the discharge produced takes the form observed in figure 8.

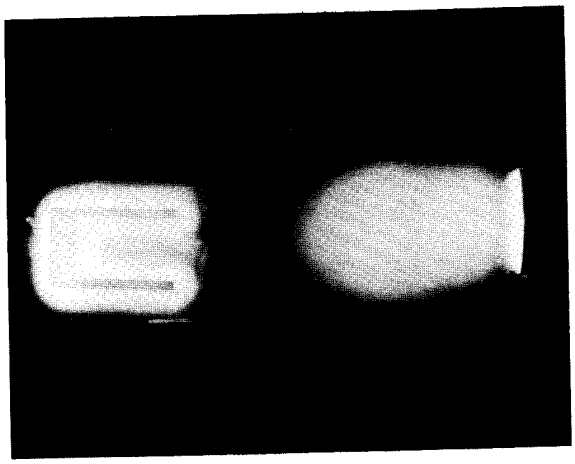


Figure 8—A low pressure glow discharge produced between two flat copper cathodes separated by a gap of 25 mm, and a flat copper anode, in helium at 10 Torr and 100 mA.

Table 4. Comparison between chemical (Chem.) and spectrometric analyses obtained with the Grimm discharge source (GDS), [93].

Sample	Limestone[a]		Granit[a]		Basalt[a]		Flintclay[a]		Argillacious limestone[b]		Pb-Ba-Glass[b]		Cement[c]	
Element	Chem.	GDS	Chem.	GDS	Chem.	GDS	Chem.	GDS	Chem.	GDS	Chem.	GDS	Chem.	GDS
Ca	34.10	34.0	0.83	0.83	4.64	4.30	0.28	-	29.44	29.5	0.15	-	29.50	30.5
Si	3.99	4.0	33.97	34.0	22.90	23.0	27.90	28.0	6.55	6.6	30.30	30.0	6.60	6.5
Al	1.27	1.30	7.27	7.50	8.73	8.5	11.10	11.0	2.21	2.20	0.10	0.12	1.56	1.60
Fe	0.69	0.68	1.48	1.50	6.81	6.9	4.85	4.75	1.10	1.08	0.03	0.27	1.12	1.10
Mg	0.45	0.45	0.26	0.30	4.49	4.50	1.18	1.20	1.30	1.30	0.02	-	0.83	0.80
Mn	0.07	0.072	0.04	0.046	0.12	0.12	0.04	0.042	0.03	0.035	0.07	0.068		0.03
Ti	0.08	0.078	0.13	0.15	0.69	0.67	0.56	0.58	0.01	0.012	0.007	-		0.06
Na	0.16	0.12	2.88	2.90	3.27	3.25	0.94	0.87			4.25	4.25		
K	0.32	0.35	3.87	4.10	0.17	0.17	3.18	3.40			6.96	7.0		
C	10.21	10.30	0.07	0.07	0.36	0.36	0.04	0.033						

[a]Zentral Geologischen Instituts, Berlin.
[b]National Bureau of Standards, Washington.
[c]Centre d'Etudes et de Recherches de l'Industrie des Lants Hydrauliques, Paris.

In this case the discharge follows the outline of the two flat cathodes, and is otherwise identical in structure and properties with the discharge obtained when a single flat cathode is used (Fig. 4).

If the distance between the two cathodes is decreased to about 8 mm or less, the two separate cathode layers from the preceding figure 8 are seen to coalesce into a single cathode layer having a high radiation intensity, as illustrated in figure 9. This is the hollow cathode discharge. In practice, instead of using two flat cathode electrodes, a cylindrical cathode is used as illustrated in figure 10. This discharge, which occurs inside the cylindrical cavity, can carry currents of the order of several amperes at a cathode fall of several hundred volts and in a relatively cold carrier gas. The distribution of the various zones seen in the planar cathode discharge mode is present in the hollow cathode mode also. The zones are disposed in a circular manner inside the hollow cathode.

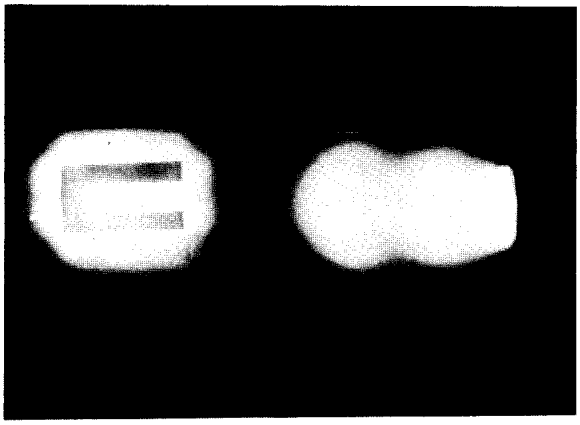


Figure 9 – Same discharge as shown in figure 8 with the two cathodes separated by a gap of 8 mm.

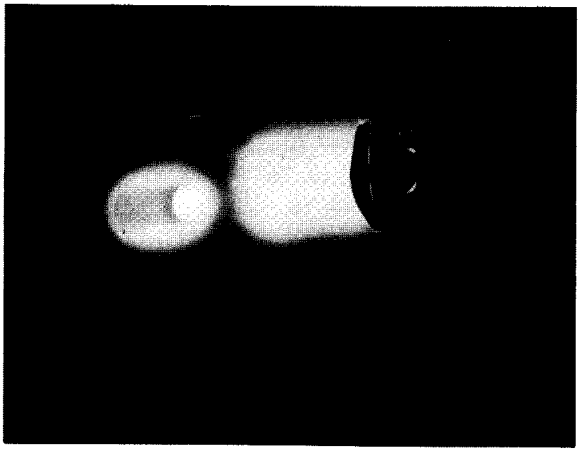


Figure 10 – Same discharge as shown in figure 9 with a cylindrical cavity as a cathode.

The low pressure hollow cathode discharge source, first described by Paschen in 1916 [253], consisted of a metallic rectangular hollow cathode and a cylindrical anode sealed in a glass vessel filled with helium at a pressure of several Torr (Fig. 11). It was adapted by Schüler and Gollnow to analytical measurements in 1937 [315], and is described in figure 12. It consists of a water cooled anode and cathode unit separated by a glass tube. The gap between the interchangeable hollow cathode and the anode electrode is of 1 mm. The hollow cathode sources used today are all derived from this basic form which was modified to a smaller or larger extent to satisfy the particular requirements of the analyst.

3.2.2 Description of an Experimental Hollow Cathode Discharge Source

One of the forms developed and used in our laboratory is illustrated schematically in figures 13 and 14. It consists of a water cooled circular anode and cathode units made of brass. The anode is provided with an inlet for the carrier gas, a fused silica window, and a terminal. An adjustable conical ring permits the distance between the anode and cathode to be varied. The cathode unit can accept an interchangeable cylindrical hollow cathode 19 mm long, with an external diameter of 6 mm, provided with a 14 mm deep and 4 mm diameter bore. The anode and cathode are separated by a ring made of 99.7 percent pure alumina provided with a lateral alumina tube for connection to a vacuum pump. The anode, alumina ring and the nylon sleeve are assembled with six nylon screws. The nylon sleeve holds the cathode unit in place, and "O" rings are used to provide a vacuum tight assembly.

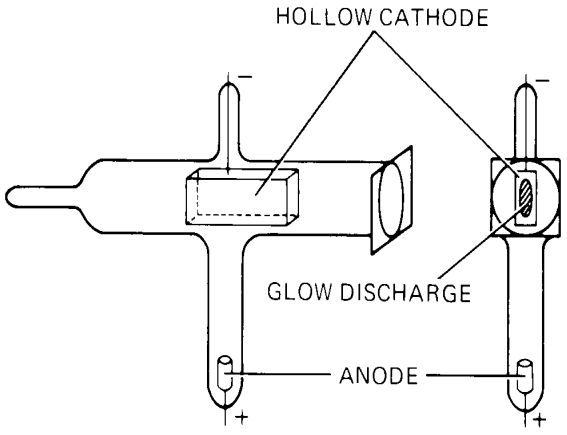


Figure 11 – Schematic description of the first low pressure hollow cathode discharge developed by Paschen [253].

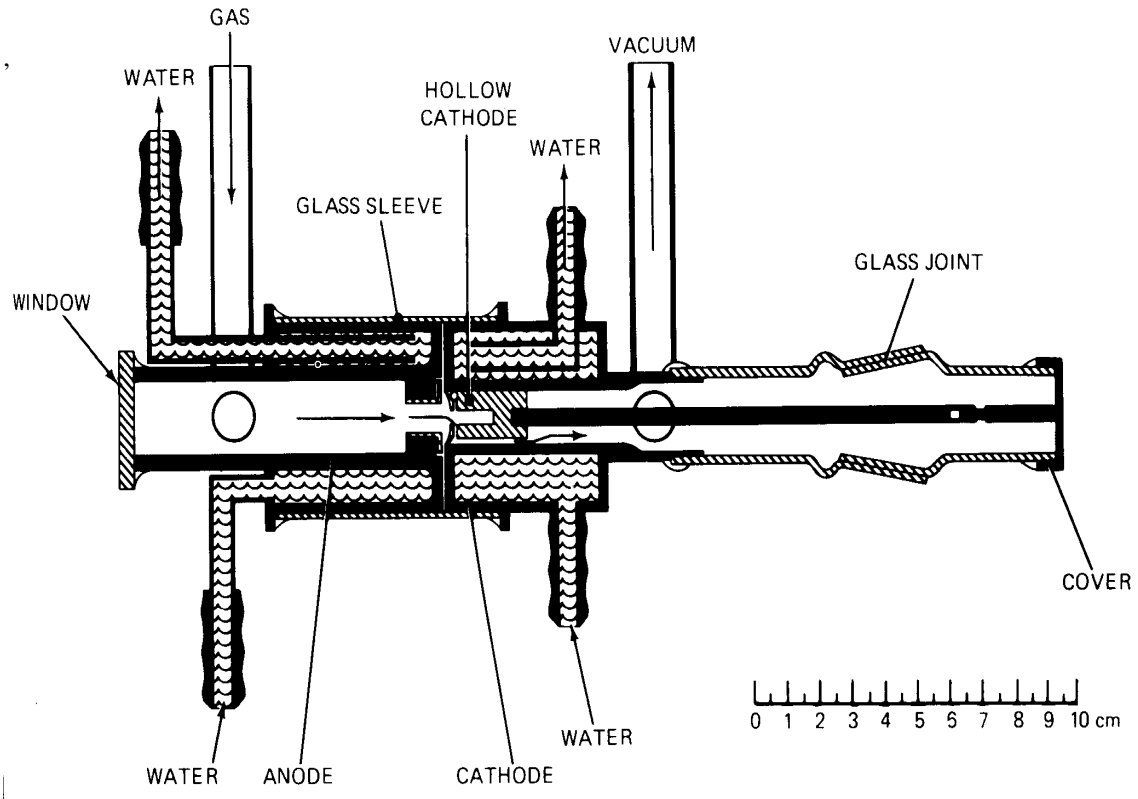


Figure 12 – A hollow cathode low pressure glow discharge source developed by Schüler and Gollnow for analytical measurements [315].

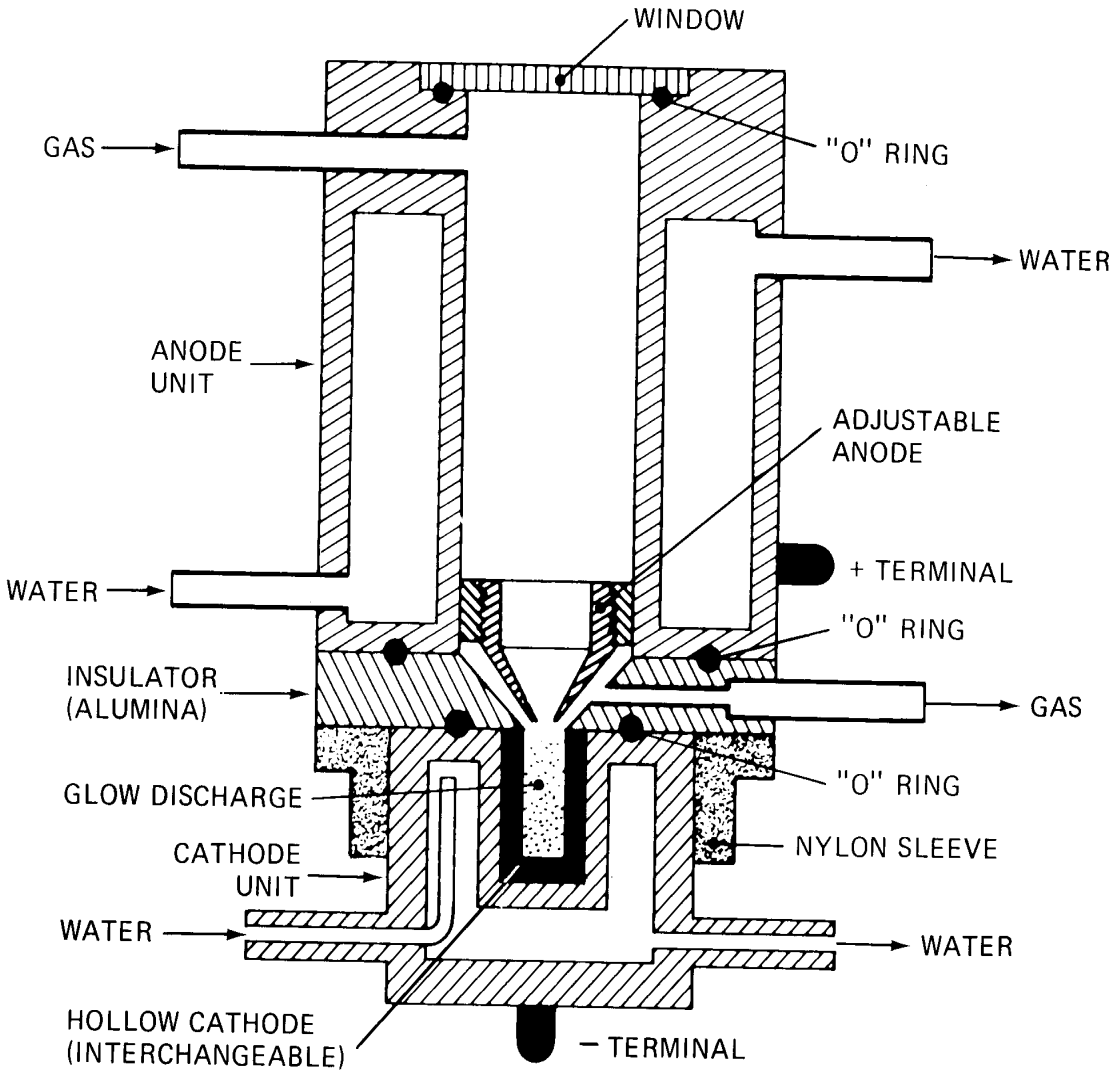
The nominal dimensions are: length and diameter of anode unit, 65 mm and 76 mm, respectively; length of alumina insulator, 12 mm; and length and diameter of cathode unit, 38 mm and 36 mm, respectively.

The cathode from (b) of figure 14 consists of a conical shaped part provided with an opening of 3 mm, and is made of pure copper in this case. Other pure materials could be used including graphite. The bottom of this conical unit is closed with a pellet 2 mm thick made from the analytical sample. This can be a solid metallic pellet or a pressed disc made of a metallic powder or a nonconducting sample mixed with a conducting powder such as pure copper. This type of hollow cathode was developed and used by Spectroscandia (Nagu, Finland) [339].

An exploded view of the unit is illustrated in figure 15 and the assembled unit is shown in figure 16. Figure 17 shows the unit in front of a Czerny-Turner 1 m grating universal spectrometer which can be operated as a scanning monochromator, a spectrograph, or a multichannel direct reading spectrometer.

The hollow cathode is connected, through a resistance of 1000 Ω and 2000 w, to a dc power supply capable of providing a current of 2.5 A and 2000 V. When the spectrometer is used in the scanning mode, the signal measuring system consists of a photomultiplier followed by a lock-in amplifier, an analog recorder and digital voltmeter. A scaler and timer unit is also available for integration of the signal over a chosen time interval. These parts are contained in the cabinet from figure 17, left. An 8-channel integrating electronic system is used in conjunction with the multichannel functioning mode, and is illustrated in figure 18 at left.

The carrier gas, usually pure argon, helium, or a mixture thereof, is supplied to the hollow cathode from corresponding high pressure bottles. The continuous flow is controlled through pressure regulators at the bottles and is limited by an individual glass capillary tube; the flow is monitored by flowmeters. A duo-seal oil vacuum pump provides the necessary vacuum which is monitored through a sensitive Bourdon-type mechanical gauge, and the hollow cathode source is connected to the gas and vacuum through off-on vacuum valves. The monitoring gauges and the valves and vacuum pump are contained in a cabinet as seen in figure 18. The current-monitoring meters – milliampmeter, voltmeter, and wattmeter – are located at the top of this cabinet which also contains the 1000 Ω, 2000 w resistor.



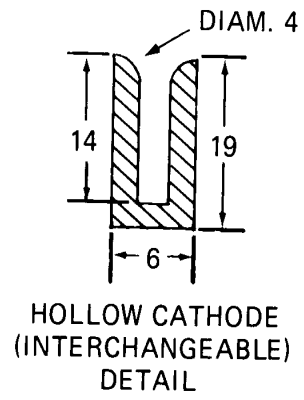


Figure 13—Experimental hollow cathode source developed in the Center for Analytical Chemistry, National Bureau of Standards. (Dimensions of detail, right, in mm.)

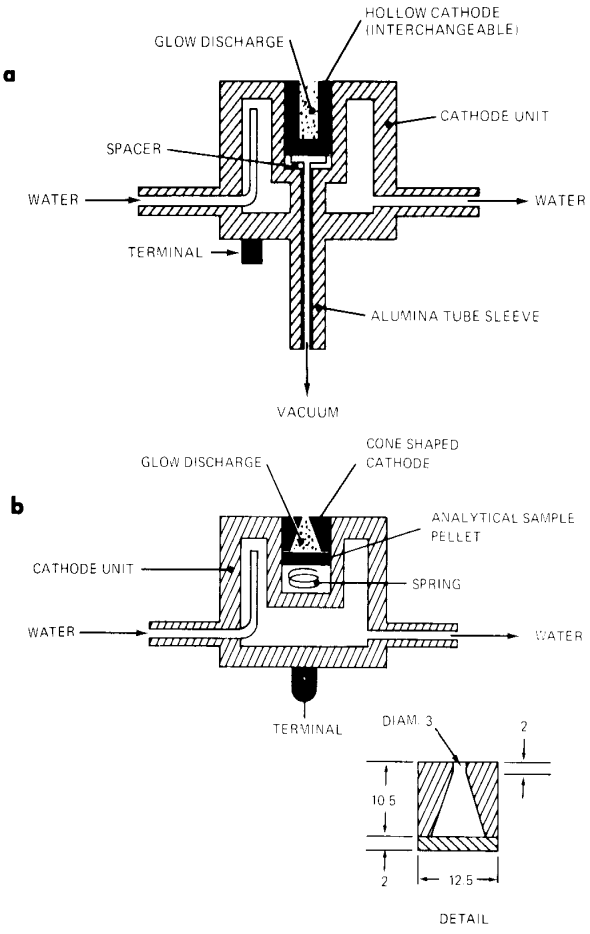


Figure 14—Alternate cathode unit (a) used in conjunction with the anode unit of figure 13. The hollow cathode proper is made from the metallic analytical sample and is interchangeable. Another alternate cathode unit, (b), also is used in conjunction with the anode unit from figure 13. The hollow cathode proper is made from two parts: a conical body, provided with a 3 mm orifice, closed by a pellet at the bottom. This pellet is the analytical sample, and can be made from a solid conducting material (metal) or pressed from a metallic powder. Non-conducting materials can be pelleted with a conducting powder such as pure copper, silver or graphite. Dimensions, right, in mm [339].

3.2.3 Characteristics of the Hollow Cathode Discharge Source

The voltage-current characteristics of the discharge were determined using an iron hollow cathode of 3.5 mm inside diameter, at various pressures, in helium, argon, and helium-argon mixture, and the results are given in table 5. From these measurements it can be seen that for a large change in current, from 50 mA to 1600 mA, the corresponding change in voltage is small, from 260 V to 430 V, when argon is used at a pressure of 10 Torr. This current-voltage relation of hollow cathode discharges is responsible for the stability of this excitation source.

Hollow cathodes can be operated at currents from several milliamperes to several amperes. Since the intensity of the radiations excited in these sources is a function of this current, the hollow cathodes used in analytical applications are supplied with currents varying from about 100 mA to about 2 A, the first hollow cathode operated at such high current being described in 1933 by Paschen and Ritschel [256]. Figure 19 describes this source which consists of a metallic cathode made, in this case, of a thick aluminum block 200 mm long provided with a transversal bore of 5 mm. A fused silica container is adapted at each end of this block through conical ground joints, and each is provided with a cylindrical anode, a quartz window, and side tubes for the carrier gas and vacuum connections; the cathode is water cooled. Under these conditions currents of up to 3 A were supplied to the hollow cathode producing an extremely brilliant source of radiation. More recently, high-current hollow cathodes were designed and used for analytical purposes by Maierhofer and associates [196], and by Thornton [362]. The current used with the source illustrated in figures 13 and 17 varied from about 200 mA to 1800 mA according to the experimental conditions.

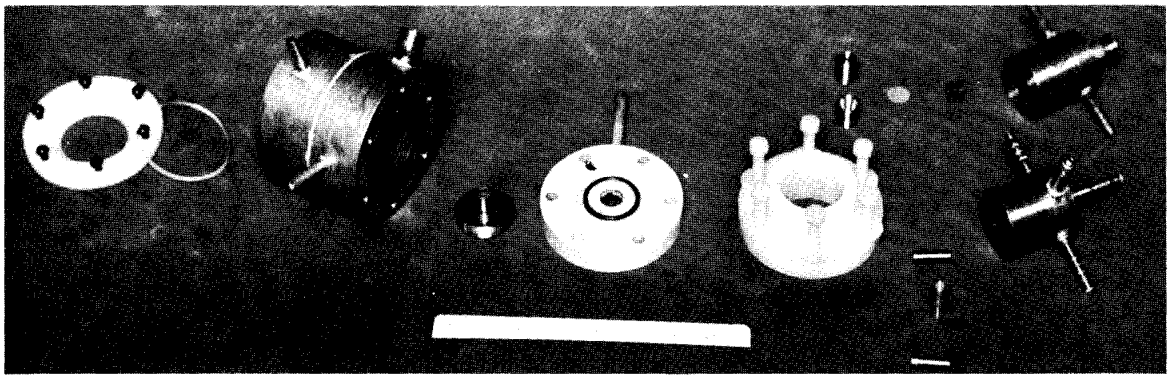


Figure 15—Exploded view of the hollow cathode source described in figures 13 and 14. From left: fused silica window with nylon retaining ring, anode unit, adjustable anode electrode, alumina insulator, nylon sleeve with six nylon assembling bolts, three cylindrical interchangeable hollow cathodes (Fe; Cu; Ag), conical hollow cathode with sample pellet, and two cathode units.

Table 5. Voltage-current characteristics for an iron hollow cathode 3.5 mm diam. in helium and argon at various pressures.

Current	Volts							
	Helium at			Argon at			Helium-Argon mixture 1:1	
A	3 Torr	6 Torr	10 Torr	3 Torr	6 Torr	10 Torr	10 Torr	13 Torr
0.050	230	240	300	240	280	260	220	280
0.10	230	240	300	240	300	300	230	300
0.20	230	240	300	400	310	310	220	315
0.30	260	240	300	480	315	330	200	340
0.40	320	230	300	540	340	330	200	360
0.50	540	230	320	620	340	360	210	370
0.60	580	240	310	700	360	380	220	370
0.70	620	240	300	760	380	380	240-320	380
0.80	640	260	300	820	390	380	340	380
0.90	680	270	300	870	400	380	360	390
1.00	720	400	300	920	410	380	370	400
1.10								
1.20	770	440	310	1000	440	400	400	400
1.30				Arc				
1.40	820	460	320		480	420	410	400
1.50								
1.60		490	340		510	430	440	400
1.70								
1.80		Arc	360		540	440	440	400

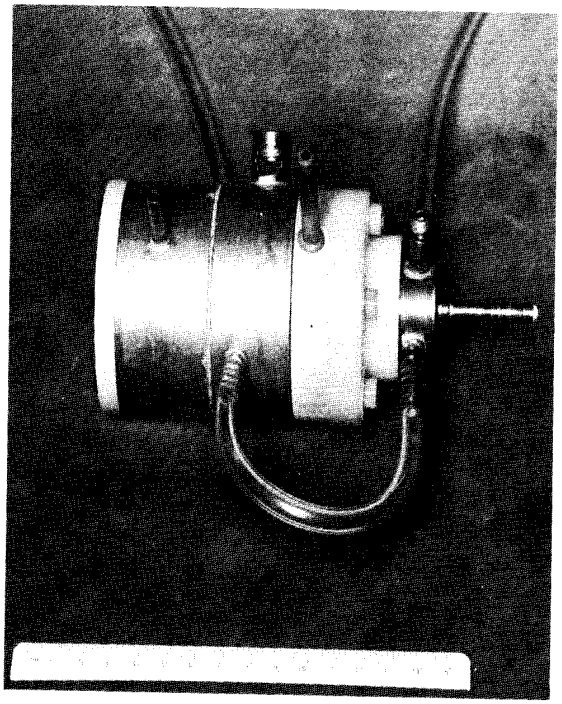


Figure 16—Assembled hollow cathode source.

The development and use of high intensity hollow cathodes is described in references *2*, *20*, *28*, *29*, *151*, *184*, *239*, *245*, *266*, and *279*.

The radiation intensities originating from the atoms of various elements, excited in a hollow cathode, are for a given set of experimental conditions a function of the current. This dependence was determined for the source described in figures 13 through 18, using a silver hollow cathode in helium at 3, 6, and 10 Torr pressure, and the results obtained are given in table 6. These data indicate that an increase of current from 50 mA to 1200 mA corresponds to an increase in the relative radiation intensity (PMV) of the Ag λ 3280.68Å emission from 0.30 V to 11.75 V, or a factor of about 40, tapering off from about 1100 mA.

The spatial distribution of this radiation inside the hollow cathode is illustrated in figure 20, after Büger and Fink [55]. The figure shows the relative intensity profiles obtained in helium at a pressure of 5 Torr and for currents from 40 mA to 1000 mA. The highest intensity was observed in the middle of the negative glow discharge, while close to the walls of the hollow cathode, the radiation intensity decreased to practically zero. This is to be expected since the cathode dark space is located between the wall of the hollow cathode and the negative glow. Similar observations were made earlier by Berezin [23].

Table 6. Relative intensity, expressed as photomultiplier voltage (PMV), for Ag λ 3280.68Å as a function of the current (mA) supplied to the hollow cathode source (HC) in helium at various pressures (P_{He}).

HC, mA	PMV P_{He} 3 Torr	P_{He} 6 Torr	P_{He} 10 Torr
50	0.11	0.25	0.30
100	0.31	0.67	0.74
150	0.51	0.86	1.50
200	0.78	1.11	1.71
250	1.03	1.32	1.86
300	1.34	1.63	2.08
350	1.75	1.94	2.39
400	2.11	2.26	2.68
450	2.45	2.61	3.04
500	2.86	3.04	3.38
550	3.20	3.48	3.76
600	3.62	3.93	4.25
650	4.07	4.37	4.57
700	4.70	4.70	4.80
750	5.32	5.21	5.38
800			5.90
850			6.30
900			6.82
950			7.44
1000			9.05
1100			10.15
1200			11.75

The radiation stability of the hollow cathode source was determined using copper, silver, and iron hollow cathodes in helium at 10 Torr and for currents of 200, 100, and 200 mA at λ 3273.96Å, 3280.68Å, and 3719.94Å, respectively. The results obtained are assembled in table 7.

The table 7 data are expressed as averages of photomultiplier voltages. These data were obtained from the tracings produced with the 1 m spectrometer described in figures 17 and 18 and operated in the analog recording mode. A preburn of 10 min was used in all cases. The stability of the photomultiplier with the associated electronics was initially determined using a stable radiation source consisting of a tritium-activated phosphor (half-life 12.5 years). Under these constant illumination conditions, a variation of the photomultiplier signal of 0.3 percent was observed over a period of 60 min. The noise observed during each measurement, expressed as photomultiplier voltage, was on the order of ±0.2 V.

The table 7 data demonstrate the excellent stability of the hollow cathode discharge which is capable of producing and maintaining a radiation intensity over a time period of 20 min with a relative standard deviation of not more than 1.6 percent for a single measurement.

The effect of the sputtering process on the surface of

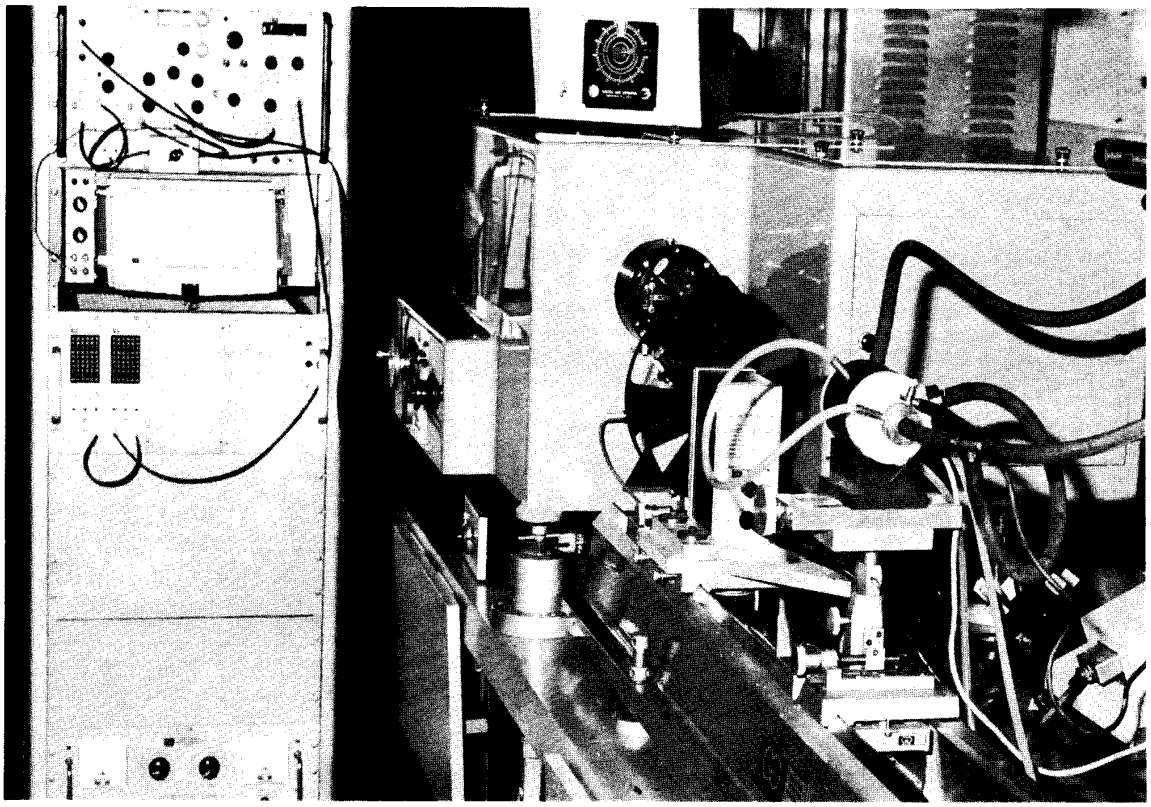


Figure 17 – Hollow cathode unit from figure 16 under functioning conditions on an optical bench in front of a 1 m Czerny-Turner spectrometer. From left: console with power supply for the photomultiplier tube; the preamplifier, amplifier and lock-in amplifier; and the digital voltmeter, analog recorder and time-scaler unit.

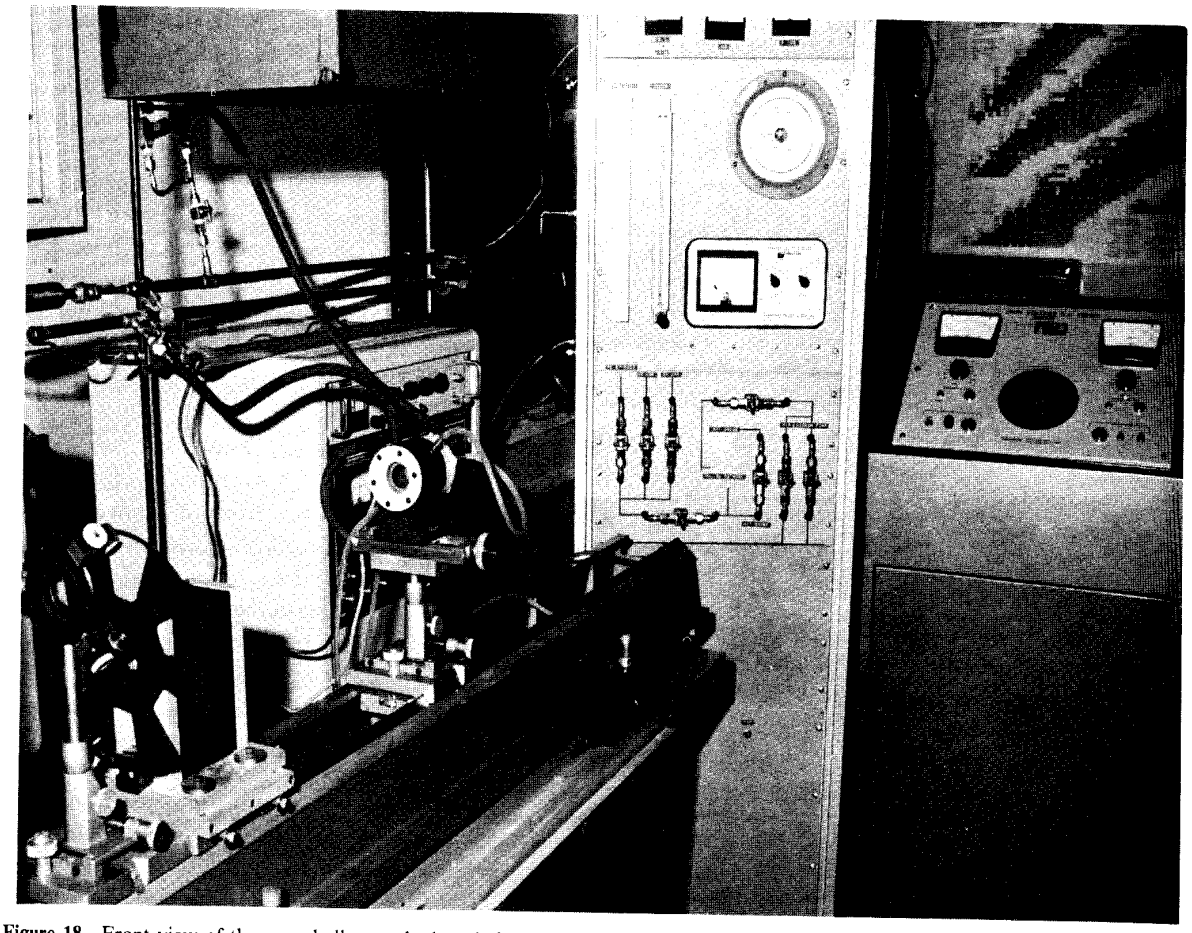


Figure 18—Front view of the same hollow cathode unit from figure 17. From left: Lock-in light chopper, hollow cathode unit, 8-channel simultaneous direct reading system, console with current and gas monitoring meters and vacuum control valves, and dc power supply for the hollow cathode.

Table 7. Stability of the radiation intensity, expressed as photomultiplier signal average (V), determined for a copper (Cu), silver (Ag), and iron (Fe) hollow cathode operated in helium at 10 Torr and a current of 200, 100, and 200 mA. The measurements were taken at time intervals of 100 s after a preburn of 10 min.

Time, s	V		
	Cu	Ag	Fe
0	8.43	8.13	6.00
100	8.43	8.15	6.05
200	8.33	8.15	5.97
300	8.20	8.17	6.00
400	8.17	8.20	5.95
500	8.23	8.20	5.90
600	8.19	8.20	5.95
700	8.09	8.19	5.87
800	8.07	8.17	5.85
900	8.10	8.27	5.85
Aver	8.22	8.18	5.94
σ	0.13	0.04	0.07
% σ	1.6	0.5	1.2

the cathode was studied recently by Jäger and Blum [156] and by Harrison and associates [72] who used copper, stainless steel, and graphite discs in helium, neon, and argon, at various gas pressures and discharge currents and for various sputtering times. After exposure to the discharge, the metal surface was examined with a scanning electron microscope using magnifications up to 5000 times. Different erosion patterns were observed for helium, neon, and argon, indicating a more pronounced change for argon which produced a surface having a "conical structure 20 to 30 microns high," and a heavier sputtering. When the sputtering time was extended to 15 hours in argon and under a current of 200 mA, the initial cylindrical shape of the hollow cathode was changed progressively into one or several successive bulb-like cavities (also see references 170 and 388). Examination of various parts of the cavity revealed different erosion patterns. It is interesting to compare these results with those obtained by White who studied the potential distribution in an ideal spherical hollow cathode cavity [388].

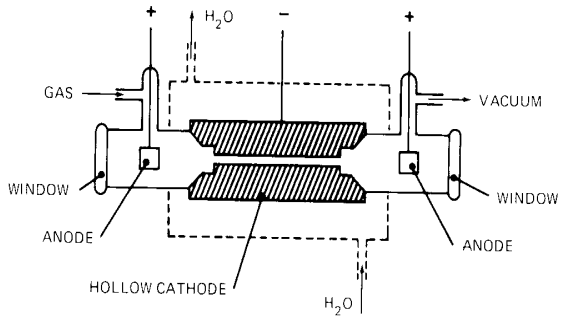


Figure 19 – High-current hollow cathode source of Paschen-Ritschel [256].

Jäger and Blum have observed the conical structure mentioned above and have concluded from their study [156], using gold and brass cathodes, that the removal of the sample material depends on crystal structure and orientation, and that there are no signs of surface melting. They also concluded that the preburn time is an essential parameter for obtaining an equilibrated sputtering surface and good analytical results. The preburn time should be established experimentally for every type of sample.

Due to the excitation conditions prevailing in the low pressure glow discharges, the spectra excited in the hollow cathode discharge are characterized by radiations with narrow spectral bandwidth and are practically free of self-absorption under the experimental conditions used to produce and observe the radiations. An example of the spectra excited with the hollow cathode from figures 13 and 14, using a copper and a silver cathode, is illustrated in figure 21 in comparison with the spectra from the same metals excited in a dc arc. The hollow cathode was operated in argon at a pressure of 4 Torr, a current of 500 mA, and an exposure time of 60 s. The dc arc was operated at a current of 8 A in air and the exposure time was 5 s. Both spectra were recorded with a 3 m concave grating Eagle spectrograph, using a 6 step rotating sector, on Eastman Kodak 33 plates. The self-reversal of the resonance lines of copper and silver is clearly visible for the radiations excited in the arc, and the lines are wide and ill-defined. The same lines obtained with the hollow cathode are narrow, well-defined, and free of measureable self-absorption.

The general aspect of the spectra excited in low pressure glow discharges also exhibit a different intensity distribution when compared with those obtained in conventional arcs and sparks. These differences have led E. W. Salpeter to produce, in collaboration with the RSV Company, an atlas of spectra of the noble gases, He, Ne, Ar, Kr, and Xe from λ 500Å to λ 4000Å, and that of the following chemical elements: Fe, Co, Cr, Mo, Nb, Ni, Ta, Ti, Cu, Be, Ca, Si, Hg, Zn, Pb, Bi, Sb, S, Sn, As, Mg, Cd, Ag, Au, Ir, Pd, Pt, Rh, Ru, Al, Hf, Mn, Se, Te, V, W, and Zr, from λ 1500 Å to λ 4000Å. The excitation source used to produce the spectra was the Grimm glow discharge lamp manufactured by RSV. The atlas was produced in 1971 to 1973 and is divided into five parts. It can be obtained from the Specola Vaticana, Cita di Vaticano, Italy [305].

An atlas of the emission spectrum of uranium excited in a hollow cathode discharge is given in reference *172*.

3.2.4 Analytical Applications

The energy, expressed in electron volts (ev), required to excite radiations from the neutral atoms of all known chemical elements, varies from one of the lowest values of 1.426 ev for uranium to the highest value of 21.215 ev for helium. Helium is one of the supporting gases used currently to produce low pressure glow discharges, and is strongly excited in these discharges to emit the radiations from its neutral and the singly ionized atoms (40.811 ev). Hence, the energy available in a hollow cathode discharge is largely sufficient to excite all known chemical species and produce radiations origi-

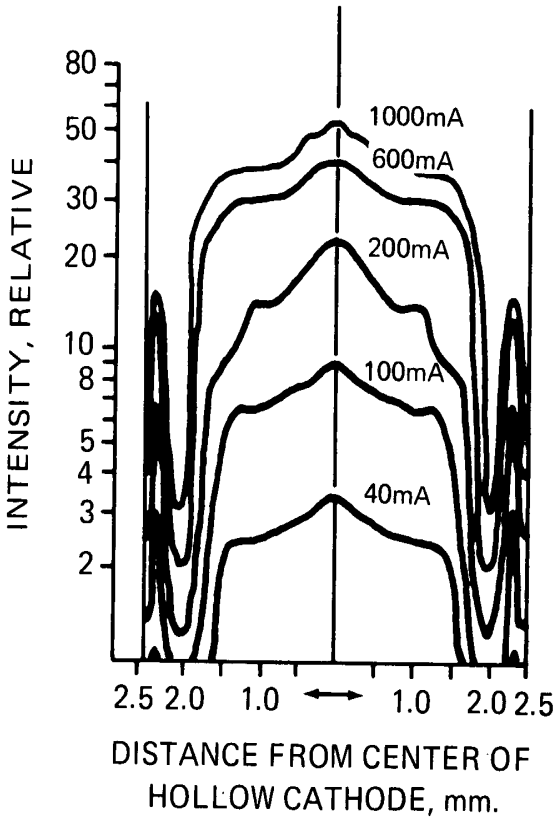


Figure 20 – Radiation intensity distribution in a hollow cathode. After Büger and Fink [55].

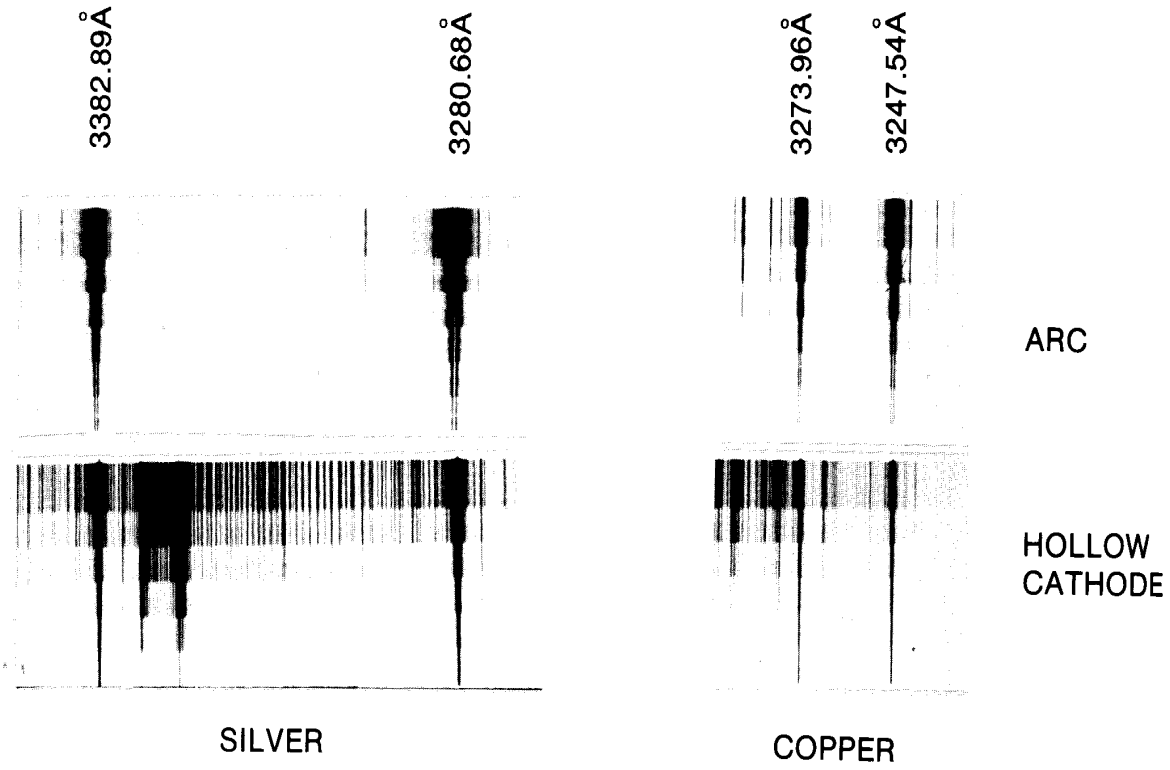


Figure 21—Spectra of Ag and Cu excited in a dc arc and a hollow cathode.

nating from the neutral and ionized atoms as well as from their molecules.

The hollow cathode discharge was initially used by Paschen to produce and study the fundamental characteristics of the spectra of aluminum [254]. Schüler and associates have extended these investigations to the examination of the hyperfine structure of the spectra from rare earths, and of elements available in milligram quantities such as the artificially produced radioactive materials [311, 312, 314, 315, 317, 318, and 322]. The excellent spectral characteristics of the discharge are related to the fact that the experimental parameters of the discharge, such as the nature, pressure, and flow of the sustaining gas, current, discharge tube and analytical sample geometry, can all be controlled. This has caused Schüler to recommend its use as a source of excitation in analytical spectroscopy.

Since then, the hollow cathode discharge has been applied extensively to various analytical problems including isotopic analyses and trace element analyses for practically all chemical species, including the halogens, in various matrices, in solid, liquid, and gaseous form, and for electrically conducting and non-conducting materials.

Some of these applications will be discussed here using data available from the scientific literature. Results obtained in our laboratories will also be presented. Further analytical use of the hollow cathode will be found in the numerous publications assembled in Section 5, Collection of References to Works on Low Pressure Glow Discharges, and to its addendum, Subsection 5.1.

The detection sensitivities obtainable with hollow cathodes depend greatly on the experimental parameters; therefore, the data given here should be considered only as an order of magnitude. The detection limits for a number of chemical elements are given in table 8 after Korovin [175]. Further measurements, published by Zilbershtein and associates [398, 399, 400], indicate that an obsolute sensitivity of 3 to 5×10^{-10}g can be obtained for Ag, Mn, and Cu; 6×10^{-10}g for Ga and In; 3 to 5×10^{-9}g for Al and Ni; and 6 to 7×10^{-9}g for Mg and Fe, in a silicon matrix, using an excitation current of 800 to 900 mA for a burn of 2 min.

Webb and Webb [381, 382] have used a hollow cathode to determine gases in metals. Their results are given in table 9; the detection limits are given in table 10.

A hollow cathode was used by Birks [29] to determine the halogens, fluorine, chlorine, bromine, and iodine, for which the following detection limits were found: 0.25 μg, 1 μg, 5 μg, and 2.5 μg respectively.

Thornton has used a high temperature hollow cathode source similar in design to that described by Webb and Webb [381, 382] to analyze steels and high temperature alloys for trace elements [362]. The samples

Table 8. Absolute detection limits for 22 chemical elements, expressed in nanograms, after Korovin [175].

Element	Wavelength, Å	Hollow cathode	Copper spark	dc arc carrier distillation
Al	3092.7	10	10	500
Ag	3280.7	0.03		5
B	2497.7	1	10	1
Be	3130.4	0.03	0.2	10
Cd	2288.0	30	200	7
Co	3453.5	0.3	50	100
Cr	2835.6	1	5	300
Cu	3247.5	0.03		30
Fe	2599.4	3	50	100
Ga	2943.6	0.03	100	
K	7664.9	10	10	200
Li	6707.8	0.1	0.2	10
Mg	2852.1	0.3 (~0.0001)	1(0.1)	50
Mn	2794.8	0.03	2	100
Na	5889.9	0.03	10	50
Ni	3050.8	1	10	200
P	2535.6	30	2000	5000
Pb	2833.1	10	5	100
Sb	2528.5	100	500	1000
Si	2881.6	1	10	300
Sn	2840.0	10		100
Zn	3345.0	3	200	2000

Table 9. Determination of nitrogen, oxygen, and hydrogen in metals [382].

	Steel, NBS Standards				Uranium carbide				Copper		Tungsten			Zirconium	Zircaloy	
Gas	8i	101E	343	125	A	B	C	D	1	2	1	2	3		A	B
Nitrogen, certified	0.018	0.039	0.074	0.002	0.051	0.037	0.037	0.022								
percent found	0.0175	0.034	0.072	0.0055	0.051	0.048	0.035	0.018								
Oxygen, certified					0.09	0.20	0.07	0.026	290	150	5.5	35	22			
percent found					0.12	0.20	0.06	0.024	295	160	7.3	25	20			
Hydrogen, certified														46	140	150
ppm found														46	133	143

were loaded in graphite hollow cathodes and were excited in helium with currents from 0.2 A up to 1.4 A and an exposure time of 5 min. The results obtained in the determination of trace elements at the part-per-million level in various metals and alloys are given in tables 11 and 12, in comparison with accepted values. It is interesting to note that the internal standard used in these determinations was helium at λ 2945.11Å. Various factors which affect the sensitivity and precision as well as matrix interferences are also discussed by Thornton in the same paper.

The hollow cathode discharge source described in

Table 10. Limit of detection of gases in metals in μg [382].

Material	Oxygen	Nitrogen	Hydrogen
Steel	0.35	0.55	
Uranium Carbide	1.5	2.5	
Tungsten	0.65		
Copper	0.75		
Zirconium			0.05

Table 11. Analysis of various samples with constant trace-element additions [362].

Sample No.	Material		Element concentration found, percent										
			Bi	In	Ga*	Sn	Pb	Tl	Sb	Zn*	Ag	Te*	As*
R3393	Nickel	Accepted value	0.0009	0.0010	0.001	0.006	0.0014	0.0014	0.0013	0.001	0.0011	0.001	0.01
		Hollow cathode	0.0012	0.0010	0.0012	0.006	0.0013	0.0016	0.0018	0.0009	0.0009	0.0012	0.014
R3394	Cobalt	Accepted value	0.0008	0.0011	0.001	0.006	0.0014	0.0004	0.0020	0.001	0.0010	0.001	0.01
		Hollow cathode	0.0010	0.0009	0.0013	0.006	0.0012	0.0006	0.0021	0.0007	0.0018	0.0014	0.012
R3395	Iron	Accepted value	0.0008	0.0008	0.001	0.007	0.0009	0.0008	0.0033	0.001	0.0010	0.001	0.01
		Hollow cathode	0.0010	0.0009	0.0019	0.007	0.0013	0.0010	0.0038	0.0008	0.0011	0.0011	0.013
R3396	Nickel 80%; chromium 20%	Accepted value	0.0009	0.0008	0.001	0.006	0.0014	0.0008	0.0016	0.001	0.0012	0.001	0.01
		Hollow cathode	0.0011	0.0009	0.0009	0.005	0.0012	0.0012	0.0018	0.0010	0.0010	0.0010	0.009
R3400	Nickel 40%; iron 40%; chromium 20%	Accepted value	0.0008	0.0009	0.001	0.006	0.0010	0.0008	0.0025	0.001	0.0012	0.001	0.01
		Hollow cathode	0.0011	0.0011	0.0012	0.006	0.0012	0.0010	0.0028	0.0009	0.0013	0.0012	0.010
R3401	Iron 50%; nickel 30%; cobalt 20%	Accepted value	0.0008	0.0009	0.001	0.007	0.0011	0.0007	0.0019	0.001	0.0011	0.001	0.01
		Hollow cathode	0.0009	0.0010	0.0014	0.006	0.0011	0.0010	0.0026	0.0007	0.0010	0.0011	0.010

*The "accepted" values given are the nominal additions; all other elements were determined by spectrochemical methods.

Table 12. Hollow-cathode discharge analysis of high temperature alloys [362].

Sample	Material		Element concentration found, percent										
			Bi	In	Ga*	Sn	Pb	Tl	Sb	Zn*	Ag	Te*	As*
R3385	Nickel-base alloy†	Accepted value	0.0001	0.0001	0.0002	0.009	0.0001	0.0001	0.0004	0.0001	0.0001	0.0001	0.01
		Hollow cathode	0.0002	0.0002	0.0003	0.011	0.0002	0.0002	0.0006	0.0001	0.0001	0.0002	0.0053
R3386	Nickel-base alloy†	Accepted value	0.0002	0.0002	0.0005	0.0050	0.0002	0.0002	0.0009	0.0002	0.0002	0.0002	0.005
		Hollow cathode	0.0003	0.0003	0.0006	0.0056	0.0003	0.0003	0.0011	0.0002	0.0002	0.0003	0.0051
R3387	Nickel-base alloy†	Accepted value	0.0009	0.0009	0.002	0.0014	0.0009	0.0009	0.0048	0.001	0.0009	0.001	0.001
		Hollow cathode	0.0012	0.0011	0.0026	0.0015	0.0012	0.0011	0.0056	0.0010	0.0009	0.0013	0.0016
R3388	Nickel-base alloy†	Accepted value	0.0005	0.0005	0.001	0.0026	0.0005	0.0004	0.0019	0.0005	0.0005	0.0005	0.002
		Hollow cathode	0.0006	0.0006	0.0012	0.0025	0.0006	0.0006	0.0022	0.0004	0.0004	0.0007	0.0023

*The "accepted" values given are the nominal additions; all other elements were determined by spectrochemical methods.
†Basic composition, percent: nickel 60, chromium 15, cobalt 15, molybdenum 5, titanium 2 1/2, aluminum 2 1/2.

figures 13, 14, 15, and 16 was used in conjunction with a 3 m concave grating Eagle spectrograph and the gas monitoring and power supply, illustrated in figure 18, to determine Mn, Ni, Co, Cr, Al, Si, and Cu in a series of four steel standards certified by NBS as Standard Reference Material (SRM) 1261 to 1264.

Hollow cathodes machined from each sample were submitted to a discharge of 0.8 A in argon at a pressure of 4 Torr, with a preburn of 60 s followed by an exposure of 120 s. The spectra of the four samples were recorded on a photographic plate (Kodak 33) together with an "unknown" sample which was selected from the four standard samples. The plate was processed in the usual manner and was read on a microdensitometer. Calibration curves were then established from the values found for the standard samples using iron as internal standard, and the values measured for the "unknown" sample were obtained by interpolation from these

curves. The resulting data are given in table 13 for the seven elements determined, and indicate that the average uncertainty of the analysis of about 5 percent is within the expected values which can be obtained when photographic plates and procedures are used as photodetectors and data acquisition means.

Table 13. Determination of seven elements in SRM 1262 using a hollow cathode discharge source.

Element	Certified value, percent	Found, percent
Mn	1.04	0.95
Ni	0.59	0.58
Co	0.30	0.30_5
Cr	0.30	0.28
Al	0.095	0.087
Si	0.39	0.39_5
Cu	0.50	0.51

The results from the stability tests discussed earlier indicate that an appreciably smaller uncertainty should be obtained when direct measurements are made with multichannel spectrometers using photomultipliers with integration and adequate data acquisition and processing methods available today. Such measurements are being performed at the present time, in association with J. Norris, using a 2 m concave grating multichannel spectrometer and the preliminary results seem to confirm the above statement. However, before the hollow cathode discharge can be used as a routine source of excitation in analytical spectroscopy, further investigations are needed. This author believes that the area requiring detailed studies is that of the sputtering processes occurring in the circumstances characteristic of the hollow cathode discharge mode of operation. The works cited in Section 5 under the title "Sputtering" should provide useful information on this subject.

4. Future Developments

Future developments in the field of low pressure hollow cathode discharges should aim in particular at increasing the sensitivity of analytical measurements. This sensitivity could be increased by increasing the current supplied to the hollow cathode. Currents from 20 A to 80 A were used by Ahsmann and van Benthem [6] in conjunction with a tantalum hollow cathode of special design. The ion temperature measured in the hot plasma beam produced with this source was of 20000 K to 30000 K for argon and 8000 K for neon.

The properties of high intensity hollow cathodes are discussed in a number of papers [*2, 20, 28, 29, 151, 184, 239, 266, 279*], and to our knowledge this type of discharge was not used in analytical spectroscopy.

Further increase in the current can be achieved by operating the hollow cathode in the pulsed discharge mode using pulses of the order of microseconds with amplitudes of several thousand amperes and with a repetition rate from several discharges to several hundred discharges per second. Such operating conditions have been described by Kielkopf [166] who used pulse amplitudes between 30 and 1500 A and gas pressures of 5 to 50 Torr in helium. This discharge was used to study the spectrum of triply ionized iron, aluminum, and the triply and quadruply ionized rare earths. Ion temperatures of 12000 K and electron temperatures of 15000 K have been measured for such a discharge. A similar high current pulsed discharge hollow cathode is used currently at the National Bureau of Standards by V. Kaufman to study the emission spectra of various chemical elements in the vacuum ultraviolet.

Pulsed hollow cathode discharges are also described in references *24, 60, 64, 65, 66, 67, 69, 122, 135, 141, 158, 163*, and *259*.

Superdense hollow cathode discharges have been studied also by Klyarfeld and associates [169] and by Abramovich and associates [1]. Further references to works in this field are assembled in Section 5.

The radiation intensity of a hollow cathode can be increased by providing additional energy to the discharge in the form of an electrical or magnetic field. Thus, van Gelder [114] has designed a cylindrical hollow cathode open at both ends as illustrated in figure 22. Additional excitation is provided by a stream of electrons generated by an auxiliary emitting cathode. Supplementary excitation was achieved also by Human and associates [146, 147, 148] to increase the emission from hollow cathodes, using superimposed direct current and a high frequency field. An intensity gain of two orders of magnitude was obtained by Bodretsova and associates [31] when a high frequency current was supplied to a hollow cathode. See also reference *35, 36*, and *72*.

The effect of magnetic fields on hollow cathode discharges was explored by Popovici and Somesan [271, 337, 338]. The hollow cathode used by these authors is illustrated schematically in figure 23. It consists of two opposite flat circular discs 20 mm in diameter separated by a gap of 4.5 mm and surrounded by a cylindrical anode 10 mm wide and 30 mm in diameter. The magnetic field, from zero to 3000 Oe, was applied as shown.

The intensity of the lead radiation at λ 4057.83Å was measured, under a constant current intensity (15 mA/cm^2), in Ne, Ar, Kr, Xe, and He, as a function of the magnetic field, and the results from figure 24 show that an increase by a factor of 10 was observed.

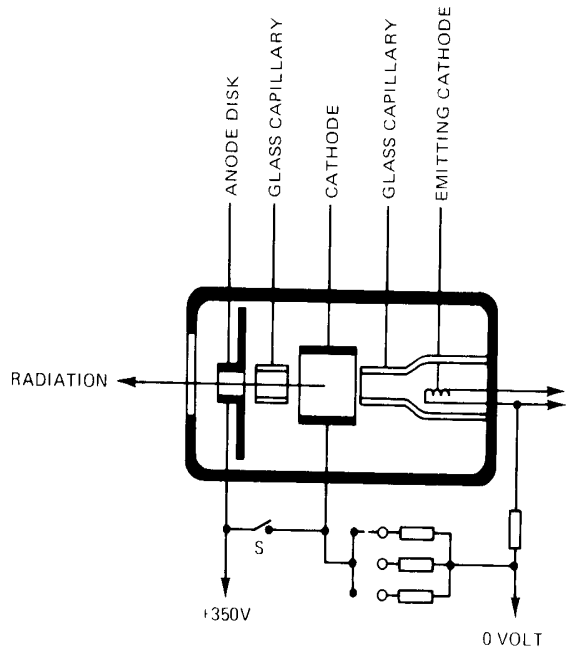


Figure 22 – High intensity hollow cathode source after van Gelder [114].

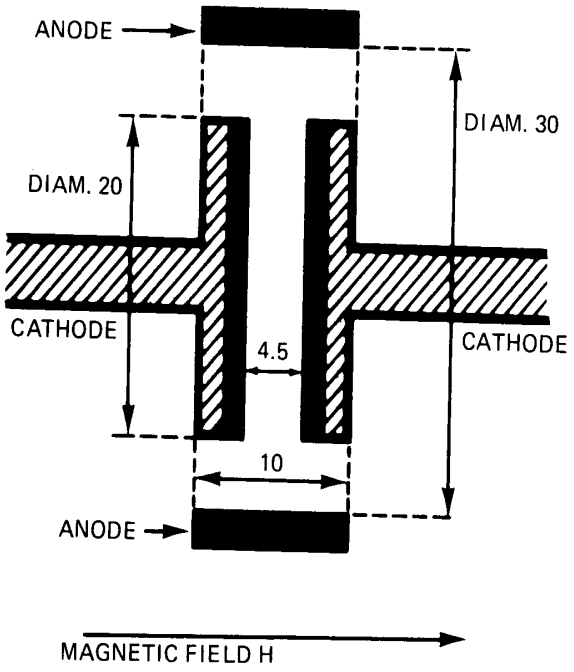


Figure 23 – Description of a low pressure hollow cathode discharge with superimposed magnetic field. After Popovici and Somesan [271, 337, 338]. Dimensions in mm.

This enhancement is significant and, if proved valid for other chemical species, should increase the use of hollow cathode discharges to the analysis of trace elements at the sub-nanogram level.

Further investigations on the effects of magnetic fields on the plasma generated in hollow cathode discharges are discussed in the Addendum to Section 5, Paragraph 15.

The author gratefully acknowledges the permission received from the various scientific journals and publications to use several illustrations and tables reproduced in this work. The sources from which the material was taken are indicated in the text. Further acknowledgment is given to the Center for Analytical Chemistry Text Editing Facility for typing the manuscript.

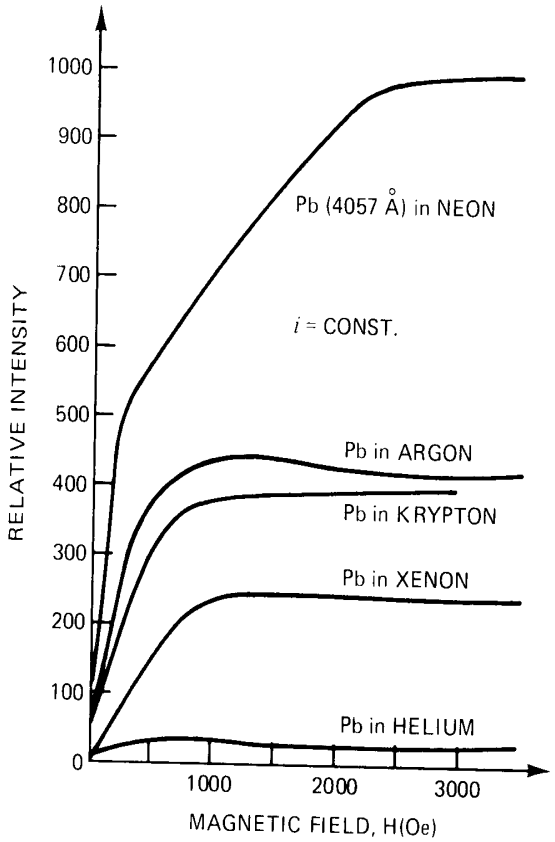


Figure 24 – Intensity of the lead radiation at λ 4057.83Å excited, under constant current, in a magnetic field and in different noble gases, using the hollow cathode source from figure 23 [271, 337, 338].

5. Collection of References to Works on Low Pressure Glow Discharges

The references in the bibliography that follows were selected with an eye toward analytical measurements.

Preceding the alphabetically arranged references is a Brief Subject Index in which the cited works are grouped under 20 subject categories. This index is intended to assist the reader in preliminarily selecting papers in his field of interest. The reader is also furnished a List of Chemical Elements.

The 400 works of the bibliography cover, roughly, the period from 1916 to 1975. In addition to this listing, a second listing offers another 290 citations. Essentially, this addendum covers the years 1975 to 1983.

In all, the base and addendum bibliographies contain 690 citations.

5.1 Brief Subject Index

1. **Glow Discharges**: 68, 89, 94, 96, 105, 138, 189, 209, 211, 213, 252, 253, 257, 365, 386.
2. **Atlas of Glow Discharge Spectra**: 305.
3. **Wavelength Standard**: 71, 341.
4. **Bibliography**: 159, 207, 208.
5. **Sputtering**: 20, 41, 72, 136, 156, 161, 232, 344, 383, 387.
6. **Fundamental Characteristics**: 12, 13, 15, 16, 33, 34, 42, 43, 49, 50, 58, 59, 60, 64, 79, 80, 81, 82, 89, 95, 101, 119, 120, 121, 132, 135, 179, 188, 191, 192, 222, 229, 233, 240, 242, 243, 245, 246, 253, 284, 309, 310, 333, 346, 347, 375, 376, 388, 389, 396.
7. **Excitation Phenomena in Hollow Cathodes**: 2, 3, 7, 12, 13, 14, 15, 16, 17, 19, 23, 24, 32, 35, 36, 37, 38, 39, 51, 53, 62, 67, 75, 79, 80, 81, 84, 87, 89, 91, 99, 108, 112, 117, 118, 120, 121, 124, 131, 133, 134, 137, 144, 145, 158, 162, 166, 169, 173, 187, 188, 191, 192, 195, 199, 224, 225, 229, 230, 231, 242, 244, 246, 247, 248, 249, 250, 251, 253, 254, 255, 256, 258, 270, 271, 272, 276, 278, 280, 281a, 285, 286, 302, 304, 306, 307, 308, 311, 314, 325, 329, 330, 336, 340, 346, 347, 350, 353, 355, 356, 357, 368, 369, 371, 373, 384, 388, 391.
8. **Excitation of Molecular Spectra**: 62, 277, 283, 313, 316, 319, 320, 321, 323, 324.
9. **Isotopic Analysis and Fine Structure**: 8, 9, 30, 43, 44, 46, 48, 63, 88, 102, 103, 104, 107, 113, 122, 164, 168, 172, 174, 180, 181, 182, 183, 184, 185, 186, 230, 235, 236, 241, 253, 282, 292, 312, 317, 318, 322, 335, 340, 345, 364, 365, 366, 367, 374, 385, 389, 392, 393, 395, 397.
10. **Instrumental Characteristics**: 40, 45, 47, 59, 60, 61, 65, 69, 70, 72, 74, 75, 76, 83, 85, 90, 92, 100, 106, 109, 110, 115, 125, 126, 127, 141, 143, 149, 150, 158, 159, 160, 163, 165, 178, 190, 193, 194, 200, 201, 202, 204, 209, 211, 212, 214, 215, 227, 237, 261, 263, 264, 268, 269, 273, 274, 275, 281, 293, 294, 315, 318, 322, 326, 327, 328, 334, 339, 342, 343, 344, 348, 349, 350, 351, 352, 354, 358, 359, 360, 363, 372, 375, 377, 378, 379, 380, 388, 390, 394.
11. **Excitation of Chemical Elements**: 5, 10, 25, 26, 27, 28, 32, 40, 41, 53, 67, 69, 97, 98, 117, 118, 124, 125, 173, 175, 190, 193, 194, 203, 218, 262, 263, 264, 266.
12. **Analytical Applications**: 5, 11, 21, 22, 25, 26, 27, 29, 40, 41, 52, 53, 54, 56, 57, 66, 73, 85, 86, 92, 93, 97, 98, 116, 122, 123, 138, 139, 140, 142, 149, 150, 151, 152, 153, 154, 155, 157, 163, 164, 171, 176, 177, 197, 198, 205, 206, 209, 210, 211, 212, 214, 216, 217, 219, 220, 221, 223, 225, 226, 227, 228, 234, 236, 238, 239, 241, 247, 248, 249, 250, 259, 260, 265, 266, 267, 279, 288, 289, 290, 291, 294, 295, 296, 297, 298, 299, 300, 301, 303, 314, 315, 331, 332, 362, 370, 380, 381, 382, 394, 398, 399, 400.
13. **Planar Cathode [Grimm Source]**: 85, 86, 93, 128, 129, 130, 226, 288.
14. **Hollow Cathode as Atomizer for Atomic Absorption**: 124, 152.
15. **High Intensity Hollow Cathodes**: 1, 6, 55, 56, 57, 58, 114, 166, 167, 169, 170, 196, 209, 211, 212, 256, 330, 334, 335.
16. **Pulsed Hollow Cathodes**: 18, 76, 77, 78, 166, 167, 195, 275, 287, 329.
17. **Hollow Cathode in a Magnetic Field**: 271, 337, 338.
18. **Hollow Cathode-RF Discharge Association**: 31, 146, 147, 148.
19. **High Pressure Glow Discharge**: 95, 111, 361.
20. **Lasers and Hollow Cathodes**: 4, 10.

5.2 Listing of Chemical Elements

References	Element
[5]	Se, As, P, S, I
[9]	Pu
[11]	nuclear fuels
[21]	alloys
[22]	S, Cl, F, Br, I
[25]	S, Cl, F
[26]	S, Cl, F
[27]	deuterium
[29]	F, Cl, Br, I
[48]	Li
[52]	F

[56]	He, Ar, N, CO_2
[57]	I
[66]	Cl, F
[73]	B
[86]	Cu, Fe, Mg, Mn, Si, Ti, Zn
[93]	Si, Ca, Mg, Mn, Fe, Al, Ti, Na, K, P, S, C
[97]	Mg, Zn, V, Cr
[98]	F, Cl, As
[116]	F, Cl, B, Li, Na, K, Rb, Cs
[123]	Mo, Ru, Rh, Pd
[129]	Be, Si, Fe, Mg, Cr, Mo, Al, Pb
[140]	Au
[142]	Pb, Cu, B, Sn
[151,153]	Zn, Cu, Mg, Mn, Ca, Sr, Cr, Fe, Co, Ni, Al, Ag, Ga, In, Tl
[154,155,157]	Au
[163]	F, Cl
[171]	Ar, N
[176]	Cl, F
[194]	F, Cl, S
[197]	As
[198]	I
[203]	Na, K, Tl, Hg, Fe, Co, Ni
[205]	Cd, Mn, Sb, Fe, Mg, Pb, Sn, Ni, Bi, Al, Cu
[206]	Li
[210]	F, Cl
[219,220,221]	I
[228]	N
[234]	Ag, Al, As, B, Be, Bi, Cd, Cr, Cu, In, Mg, Mn, Na, Pb, Sb, Sn, Tl, Zn, Ni, Si
[238]	Ag, Cu, Pb, Bi, Cd
[239]	Ag, Bi, Cu, As, Ni
[259]	Cu, Ag, Mn, Mg, Pb, Bi, Ga, Zn, Cr, Sn, Ni, Sb
[260]	Al, Fe, Ca, Co, Si, Mg, Mn, Cu, Na, Ni, Ag, Cr
[262]	Cu, In, Sn, Al, Ga, Mg, Ni, Cr, Pb, Mn
[266]	V, Mo, Ta, Zr, Ti
[267]	Al, Ge, Fe, Bi, Au, In, Co, Mn, Cu, As, Ni, Pb, Ag, Sn, Tl, Cr, Zn, Ga, Sb
[283]	P
[289,290,291]	O
[295]	Cd, Zn
[296]	Ge, Si
[298]	As, Sb
[299]	Se, Zn
[300]	S, Cd
[301]	Bi, Al, B
[303]	In, Ge, Cd, Tl, As, Sb, Pb, Sn, Fe, Cu, Ni, Co, Bi, Ag
[332]	Bi, Pb, Sn, Cd, Zn, Sb, Cu, Mg, Mn, Fe, Al, Cr, Ni
[335]	N, O
[362]	Bi, In, Ga, Sn, Pb, Tl, Sb, Zn, Ag, Te, As
[370]	N, O
[381]	O
[382]	O, H, N
[393]	N, O, H
[398]	Ag, Mn, Cu, Ga, In, Al, Ni, Mg, Fe
[399,400]	Al, Ga, Fe, Ag, Mn, Cu

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5.4 Addendum—Preface

The 290 references assembled in the addendum for the most part cover the period from 1975 to 1983. They are in alphabetical order and are numbered in italic type to differentiate them from the 400 references of the base bibliography. Several references dating before 1975 escaped the base bibliography and are included in the addendum. The addendum, like the base listing, is preceded by a Brief Subject Index and a Listing of Chemical elements.

5.5 Brief Subject Index (Add.)

5.6 Listing of Chemical Elements (Add.)

Reference	Element
[*1*]	Al
[*3*]	H
[*6*]	Bi, In
[*16*]	Li
[*17*]	I

[19]	Ca
[25]	Rare Earths
[26]	Rare Earths
[34]	Cu, Al
[38]	Ga
[49]	He, Cd
[51]	As, Se
[56]	Ba, Sr
[58]	H
[64]	Cu, Fe
[65]	Zn
[66]	Al
[67]	Al
[69]	Cu
[70]	Mo, Fe, Si
[73]	Sr
[75]	Ar
[76]	Ar
[77]	As
[79]	Li
[81]	U
[87]	Cu
[90]	Cs
[102]	Hydride
[108]	He
[109]	He
[113]	N, Co
[118]	Mg
[119]	Mg
[122]	Sb, Bi, Ag, Cu
[123]	He
[128]	Te
[133]	Ni, Co
[135]	He
[136]	Au
[137]	Ti
[139]	Co, N
[140]	He
[142]	Alkaline Elements, Mg
[143]	Group IV Elements
[147]	Ge, Se, Cd
[149]	Cd
[152]	F, U
[164]	Ba, Cd, Cu
[166]	Dy
[167]	Zn
[172]	U
[173]	Cd
[174]	Al-ammonium Alums
[175]	Al
[176]	Ti
[178]	U
[179]	Graphite
[189]	Cd, Na
[190]	W, S, P
[191]	Alkali Metals
[192]	Alkali Earth Elements
[194]	In, Ga
[198]	W, S, P, Zn, Cd
[199]	Cr
[201]	Cd
[202]	Si, Ge
[203]	S, Cd, Se
[204]	Si
[205]	Rare Earths
[206]	Rare Earths
[208]	B
[209]	Ge
[214]	Si
[216]	Cr, Ti
[218]	Pt
[221]	He, Cu, Ag
[222]	Cu
[223]	Cu
[224]	Si
[228]	Ga
[233]	U-235/U-238
[234]	U-235
[236]	Ne, Zn
[237]	Cu, Ag
[239]	Cu
[244]	Au
[245]	Steels, Nickel-base and Ferroall
[259]	Xe F, Xe Cl
[262]	Sr, Ba
[263]	Xe Cl
[268]	Cl, Xe Cl
[270]	Al, Cu, Ni hydrides and deuterides
[271]	Cu
[273]	Am, Cm
[274]	Am, Cm
[277]	H
[283]	Cu
[285]	Cu

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An Iterative Calibration Curve Procedure

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Calibration curves are an important part of many measurement processes. The user of a fitted calibration curve must know its precision and accuracy. These are determined in a timely fashion using the data iteratively. This paper gives a method that divides the data into training and test groups. The test group is iteratively checked to see that a prechosen nominal confidence interval probability of coverage is met. If on the basis of this check the calibration experiment is completed, the nominal probability level is shown to still be valid.

Key words: constants; measurements; observations; probability; statistics; statistical methods.

1. Introduction

Calibration curves are an important part of many measurement processes. The user of a fitted calibration curve must know its precision and accuracy [1][1], and these are determined in a timely fashion by using the data iteratively. This paper gives a method that divides the data into training (calibration curve-producing) and test (check) groups. The test group is iteratively checked to see that a prechosen nominal confidence interval probability of coverage is met. If on the basis of this check the calibration experiment is completed, the nominal probability level is shown to still be valid.

We assume that the measurement process has negligible drift. This is only partially checked by the iterative calibration technique; of course, routine application of control chart procedures is a must [2].

It is also assumed that many measurements are taken between calibrations. Under this circumstance particularly appropriate statistical calibration procedures are found in Scheffé [3], Lieberman, Miller, and Hamilton [4], and Knafl, Sacks, Spiegelman, and Ylvisaker [5]. We concentrate on the Scheffé procedure; it is demonstrated on an engineering example in Lechner, Reeve, and Spiegelman [6].

All of these procedures produce interval estimates such that the true value is contained in $(1-\alpha)\%$ of them in the long run with probability $1-\delta$. The two probability levels α and δ are chosen by the calibrator.

In order to describe the iterative procedure, the necessary notation is given.

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[1]Figures in brackets indicate literature references at the end of this paper.

2. Notation and Method

There are two fundamental variables: Y which is a nonstandard measurement of a property and x which is an exact standard or certified value of a possibly different property. For the example in section 3, x represents the gravimetric value (mass) of liquid in a tank (fig. 1) and Y represents differential pressure.

These two variables are related by the equation $\mathbf{Y}=H\beta+\sigma\mathbf{e}$, where the terms of the equation are defined below. The other observables are Y_i^* $i=1,2,\ldots$, and they correspond to unknown x_i^*.

Here $\mathbf{Y}$ is an nxl vector of observations, H is an nxp full rank matrix whose i-th row is $\mathbf{h}_i^t=\mathbf{h}^t(x_i)=(h_1(x_i),\ldots,h_p(x_i))$, $\beta^t=(\beta_1,\ldots,\beta_p)$, $\mathbf{e}$ is an nxl vector of independent and identically distributed standard normal random variables having mean zero and covariance matrix $V(\mathbf{e})=\mathrm{I}_n$, and σ is the standard deviation. The Y_i^* are post calibration observations and the goal is to estimate their associated x_i^*; in this paper x_i^* are taken to be unknown constants.

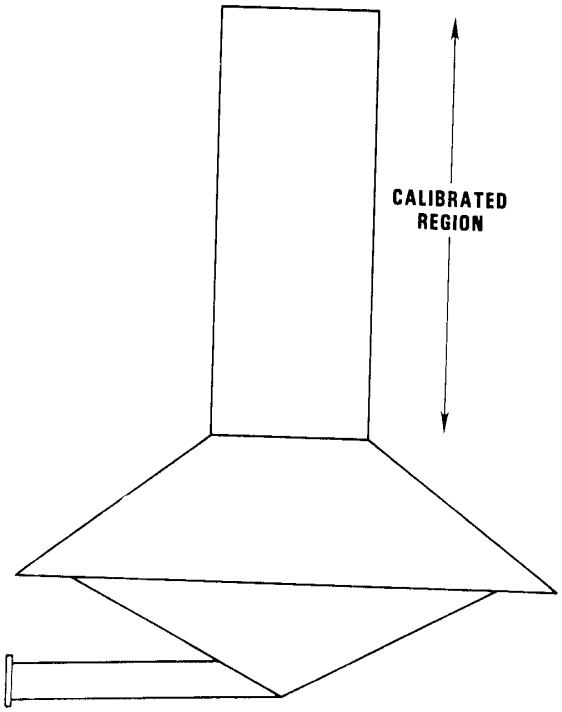

Figure 1—Calibrated tank located at NBS. A cubic model was used to correspond to linear deformation of all the tank walls.

The calibration curve is denoted by $m(x)=\mathbf{h}'(\mathbf{x})\beta$; it is taken to be monotonic. Let the least squares estimate of $m(x)$ be denoted by $\hat{m}(x)$ and its variance by $\sigma^2 s^2(x)$. Initially we assume that σ^2 is known. We discuss estimating σ^2 in section 4.

Data are nearly always collected sequentially; therefore it makes sense to analyze them sequentially. Once the measurement process is out of control additional measurements are of value only in identifying the problem. If a reasonable statistical procedure is available for iteratively analyzing the data, as is the procedure outlined in this section, then it should be used. This will help identify out-of-control situations early.

Of course the ability to detect out-of-control situations depends on the calibration design, i.e., x-values used for the calibration. Such designs have been discussed in detail for linear spline calibration curves [7]. As a byproduct of the present investigation we show the soundness of the advice in the cited work against using the exact optimal design. In fact efficiency under an assumed model and an ability to check when this model holds are competing demands.

A procedure is given for checking in an ad hoc fashion the validity of the previous assumptions. The checks are deliberately for coverage probabilities rather than directly for the assumptions, i.e., the stated $(1-\alpha)$ uncertainty level is checked. This is an indirect check on the underlying assumptions. If an assumption is marginally violated and yet the $1-\alpha$ is met, the author sees little reason to doubt the calibration procedure. If the nominal level is not met, then the calibrator is expected to at least check his measurement procedure and possibly reset his equipment. The novelty of this procedure is that if the experiment is carried to completion, the nominal levels $(1-\alpha)$, and $(1-\delta)$ remain valid.

Our procedure is as follows:

Step 1. After a reasonable amount of data is collected, the data are divided into two groups, SG1 and SG2. New data are placed in either group. Ways in which this may be done are given as comments at the end of this section. Each group should contain approximately half the data, although under some circumstances other divisions are reasonable (see section 4). The partitioning of the available data can be done randomly or according to a well chosen statistical sampling plan (see the comments at the end of this section).

Step 2. Choose the probability levels $1-\alpha$ and $1-\delta$. In order to simplify the notation, anything calculated only from the data in SG1 has subscript 1; anything calculated from all the data has no subscript.

Step 3. Using only data from SG1, determine the least squares estimate of $m(x)$, $\hat{m}_1(x)$ and its variance $\sigma^2 s_1^2(x)$.

Step 4. From the data in SG1, form the Scheffé upper and lower curves $U(x)$ and $L(x)$. The rationale is given in Scheffé [3] and Lechner, Reeve, and Spiegelman [6].

For *all* x

$$U(x)=\hat{m}_1(x)-\sigma(z_\alpha+\chi_\delta(p)s_1(x))$$

$$L(x)=\hat{m}_1(x)+\sigma(z_\alpha+\chi_\delta(p)s_1(x)).$$

Here z_α is the two-tailed α point of a standard normal; $\chi_\delta^2(p)$ is the upper δ point of the chi-squared distribution with p degrees of freedom and

$$\chi_\delta(p)=\sqrt{\chi_\delta^2(p)}.$$

Step 5 (optional). Calculate the minimum of $s_1(x)$ in the calibration region. Denote $\min s_1(x)$ by s. Redefine z_α to be the solution q of the equation

$$\Phi(q+2\chi_\delta s)-\Phi(-q)=1-\alpha. \qquad (1)$$

As explained [5], this step reduces the conservativeness of the Scheffé procedure while maintaining the validity of the probability statements.

Step 6. For each (x_i,Y_i) in SG2 check whether or not $x_i \in [L^{-1}(Y_i),U^{-1}(Y_i)]$. Let

$$T_i=\begin{cases} 1 \text{ if } x_i \in [L^{-1}(Y_i),\ U^{-1}(Y_i)] \\ 0 \text{ otherwise} \end{cases}$$

Recall both $\hat{m}_1(x)$ and $m(x)$ are linear combinations of the $h_j(x)$, $j=1,\ldots,p$. Let $\theta^t=(\theta_1,\ldots,\theta_p)$ be a vector parameter in R^p and $\theta^t\mathbf{h}(x)=\hat{m}_1(x)-m(x)$. Let $p(x,\theta) = \Phi(\theta^t\mathbf{h}(x) + \chi_\delta(p)s_1(x) + z_\alpha) - \Phi(\theta^t\mathbf{h}(x) - \chi_\delta(p)s_1(x) - z_\alpha)$. Finally denote the likelihood conditioned on SG1 and thus also on $\hat{\beta}_1$ by

$$L(\mathbf{x},\theta);\ L(\mathbf{x},\theta)=\prod_{i\in SG2} p(x_i,\theta)^{T_i}(1-p(x_i,\theta))^{1-T_i}.$$

From the likelihood $L(\mathbf{x},\theta)$, get the maximum likelihood estimator $\hat{\theta}$ for θ and compute the maximum likelihood estimator for $p(x,\theta)$, $p(x,\hat{\theta})$. Check whether or not $p(x,\hat{\theta})\geqslant 1-\alpha$ for all x in the calibration region. If for some x, $p(x,\hat{\theta})<1-\alpha$, consider the measurement process possibly defective. If for all x, $p(x,\hat{\theta})\geqslant 1-\alpha$ and the calibration experiment is not finished, collect the next data point and return to step 1.

Many scientists may not have the computer programs readily available to form the efficient maximum likelihood estimator of $p(x,\theta)$. In these cases we recommend using local averaging or otherwise smoothed estimates (see Stone [8] or Collomb [9]). In particular we recommend a nearest neighbor approach. Choose a number k and then at each point x in the calibration region average the T_i values corresponding to the k closest x_i values to x. For small samples there is little known about choosing k; however, in large samples a value of k approximately equal to $n^{2/5}$ should be satisfactory.

This procedure provides a balanced check on whether the conservativeness of the Scheffé procedure and the lack of the model holding exactly, seriously alter the hoped for uncertainty level $1-\alpha$. The bigger the sample size, the less conservative the Scheffé procedure.

Comments about **design**:

As previously stated, the Scheffé procedure is very conservative when $s_1(x)$ is large. Therefore, some of the best diagnostic information comes from data where $s_1(x)=s$. The optimal (D-optimal) design takes observations where $s(x)$ is at a maximum. Thus for a straight line the optimum design has observations only at the ends of the calibration region. Some of the best diagnostic information occurs at x-values in the middle and will be missed with this design.

Comments about **subgroups**:

Often the calibrator will have a good understanding about the possible malfunction of his measurement system. Then a choice of subgroups will be clear. He should feel free to choose as many combinations as he likes. The validity of uncertainty statements for completed calibrations remains. The check procedures are ad hoc, and if many checks are performed, he should expect some of them to indicate a possible malfunction of his system. The interpretation of these ad hoc checks requires sound scientific and engineering judgment. Some possible choices of subgroups are:

1) If we are mainly interested in detecting drift then SG1 should contain the older measurements and SG2 the newer ones. If we want to check run-to-run variability, SG1 and SG2 should not contain observations from the same run.

2) Suppose we want to check whether or not $m(x)$ has the assumed form over a subinterval $[a,b]$. Then SG1 should *not* contain (if possible) observations with x-values in $[a,b]$.

3. Analysis

We show that if σ is known all the T_i are independent of $\hat{m}_2(x)$; in this case, our iterative check does not affect the coverage probabilities when the model defined in section 2 holds.

THEOREM. *When σ is known the statistics* T_i *are independent of* $\hat{m}(x)$.

PROOF:

$T_i=1$ if and only if

$$\hat{m}_1(x_i)-\sigma(\chi_\delta(p)s_1(x_i)+z_\alpha)\leqslant Y_i$$

$$\leqslant \hat{m}_1(x_i)+\sigma(\chi_\delta(p)s_1(x_i)+z_\alpha) \qquad (2)$$

Clearly eq (2) is equivalent to $-(\chi_\delta(p)s_1(x_i)+z_\alpha)$

$$\leqslant \frac{Y_i-\hat{m}_1(x_i)}{\sigma} \leqslant (\chi_\delta(p)s_1(x_i)+z_\alpha).$$

Given the least squares estimate for β, $\hat{\beta}_2$, $E[Y_i|\hat{\beta}]=\hat{m}(x_i)$; similarly $E[\hat{m}_1(x_i)|\hat{\beta}]=\hat{m}(x_i)$.

Thus, $Y_i-\hat{m}_1(x_i)$ is uncorrelated with $\hat{\beta}$. Since the $Y_i-\hat{m}_1(x_i)$ and $\hat{\beta}$ are jointly normal the T_i are independent of $\hat{\beta}$. Q.E.D.

Suppose σ is not known but estimated independently from the calibration experiment. Then if the upper and lower bounds in Scheffé [3] are modified as he indicated the desired uncertainty statements still apply. This follows from the fact that all of the T_i are independent of $\hat{\sigma}^2$. This is not obvious to the author so the details are included.

Let T_i be modified to incorporate replacement of σ by σ_1; see Scheffé [3] for details. It is to be shown that the T_i are independent of $\hat{\sigma}^2$. Divide all sides of modified eq (2) by $\hat{\sigma}^2$. After some algebra $\hat{\sigma}_1^2/\hat{\sigma}^2$ can be written as a function of the ratio of two independent chi-squares whose sum is proportional to $\hat{\sigma}^2$. By applying standard change-of-variable techniques, it can be seen that $\hat{\sigma}^2$ is independent of this ratio. Finally $[Y_i-\hat{m}(x_i)]/\hat{\sigma}$ are uniformly distributed on a unit sphere and are independent of $\hat{\sigma}^2$. Q.E.D.

4. Example

The pressure mass calibration example is based upon data collected under the direction of J. Whetstone of NBS. The tank is of an experimental nature and is located in the fluid mechanics building at the National Bureau of Standards. The calibration curve relates pressure and mass measurements. In the region where the tank is used the calibration curve is hypothesized to be a straight line. However, due to bowing of the tank walls C. P. Reeve of NBS' Statistical Engineering Division and the author felt a cubic model was more appropriate. This model corresponds to linear deformation of all the tank walls.

The calculations made were done using the updated version of the program fully documented in Lechner, Reeve, and Spiegelman [10]. The updated program allows designation of training and test samples and automatically indicates whether or not a test point is in the calibration interval. Further information about this modification can be obtained from the author or C. P. Reeve.

The data are shown in table 1. In figure 2 residuals from the five runs are shown. Clearly run 2 is quite different from the others. However, as figure 3 indicates, the third run is also quite different from runs 1, 4, and 5.

In all cases σ^2 is estimated from the data. For the data on hand if SG1 contains any data points from run 2 then $p(x,\hat{\theta})$ is identically one. That is, the Scheffé intervals include all the data in SG2. This is true regardless of how many points are in SG1, provided it is five or more. (Note: Five is the minimum number of observations needed). If all of the points from run 2 are in SG2 then the Scheffé intervals cover none of them. In particular if SG2 contains only the data from run 2, $p(x,\hat{\theta})$ is identically zero, see figure 4.

Note that in typical cross validation procedures a fixed number of observations, usually one, is dropped out at a time and the procedure checked [11]. If this is done then the estimate of $p(x,\theta)$ is identically one. It can be shown that even if four or five observations are dropped out at one time the resulting average estimate of $p(x,\theta)$ will be nearly one. Thus, it appears that in this case purposeful choice of SG1 and SG2 is important.

Table 1. Mass-pressure calibration data.

Mass	Pressure	Run
567.004	2.06534	1
567.2	2.0655	3
567.22	2.05974	2
585.772	2.32647	4
586.091	2.32747	3
604.913	2.58939	5
604.964	2.5881	3
623.878	2.84772	3
680.441	3.62457	1
680.693	3.61958	2
699.204	3.88191	4
718.321	4.14248	5
737.333	4.39982	3
793.881	5.17109	1
794.134	5.16728	2
812.658	5.4279	4
831.74	5.68723	5
850.749	5.94467	3
907.347	6.71461	1
907.572	6.71065	2
926.108	6.97103	4

5. Conclusions and Summary

It is important to find out early whether or not a calibration procedure is in control. In particular for the example in section 3, had the new procedure been applied the experiment might have been terminated as a failure after run 3. Alternatively one additional run to compensate for run 2 may have been collected. Surely

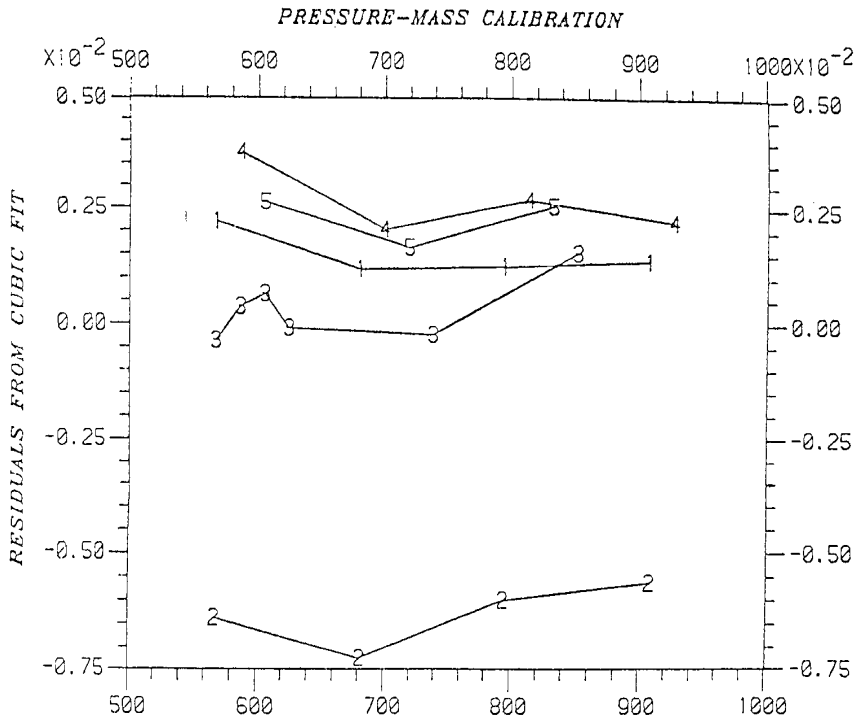

Figure 2—Residuals from runs 1-5.

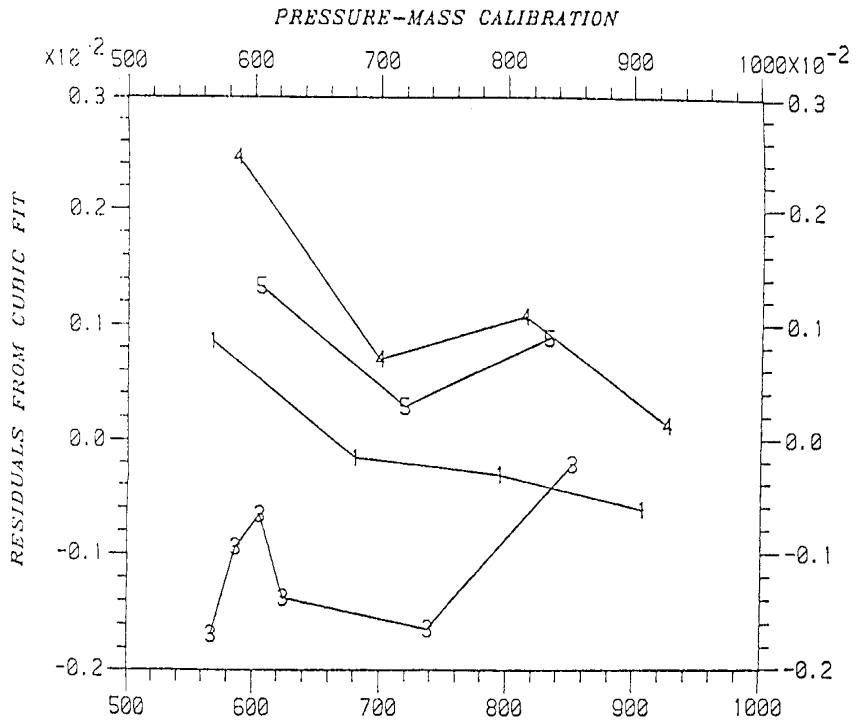

Figure 3—Residuals from runs 1, 3, 4, and 5.

something different would have been done. Clearly, too, the Scheffé procedure is conservative enough to account for some unmodeled run-to-run variation as in run 3.

Thus an iterative calibration can provide insight into the calibration procedure in a timely fashion without doing too much violence to the final uncertainty statements.

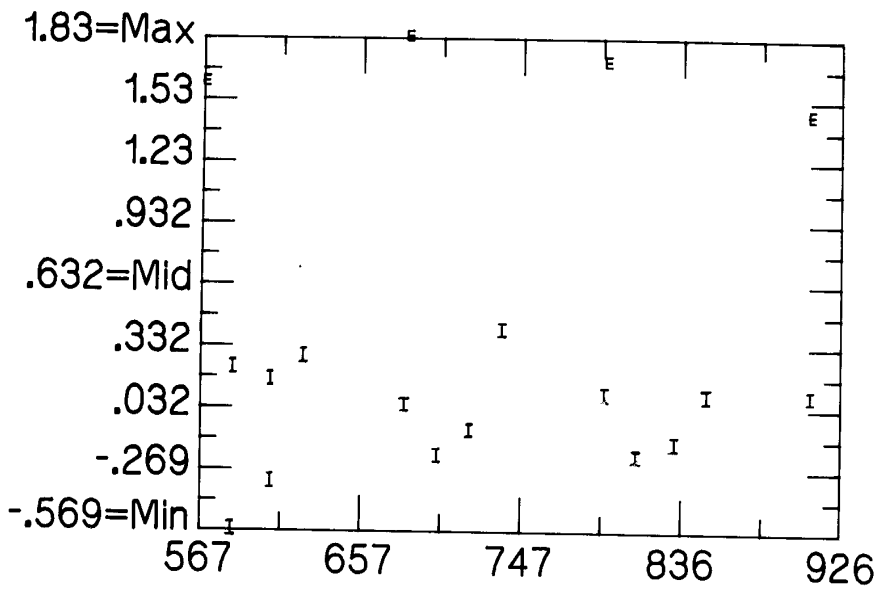

Figure 4—Summary of cross-validation results. Data from runs 1, 3, 4, and 5 are shown in SG1; data from run 2 are shown in SG2. A value bigger than 1 in absolute value indicates an x value outside the calibration interval.

Software Package:CPR*SPLINEUPDATE
Summary of Cross-Validation Results

	SG1	SG2
	X included	X excluded
Inside x C.I.	17	0
Outside x C.I.	0	4
Pct. Inside x C.I.	100%	0%

The author thanks J. Whetstone for providing the data and insight into his calibration system. The data were jointly examined with C. P. Reeve who has written a program to implement many of the procedures shown in this paper.

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Determination of the Viscoelastic Shear Modulus Using Forced Torsional Vibrations

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A forced torsional vibration system has been developed to measure the shear storage and loss moduli on right circular cylindrical specimens whose diameter can vary from 2 to 9 cm and whose length can vary from 2 to 15 cm. The method and apparatus are usable over a frequency range of 80 to 550 Hz and a temperature range of −20 °C to 80 °C.

Key words: shear modulus; torsion; vibrations; viscoelastic.

Introduction

Many methods exist for the experimental determination of the viscoelastic properties of materials. Some of these methods have been summarized [1,2][1] and those that have been used more recently appear in a collection of abstracts [3]. The method described herein, which uses forced torsional vibrations, is an updated version of previous works [4,5]. It was selected because it most easily met the requirements placed on the geometry and dimensions of the sample, a circular cylinder whose diameter ranged from 2 to 9 cm and whose length ranged to 15 cm. This wide range of sizes is a consequence of the desire to use the same sample that was previously subjected to a different kind of material properties' test over a different (higher) frequency range. The method and apparatus described subsequently is usable over a frequency range from 80 to 550 Hz and a temperature range from -20 °C to 80 °C.

About the Author, Paper: Edward B. Magrab is a mechanical engineer in the NBS Automated Production Technology Division. The work on which he reports was sponsored by the U.S. Naval Ship Research and Development Center.

[1]Figures in brackets indicate literature references at the end of this paper.

Theory

Consider the forced harmonic torsional vibrations of a right circular cylinder having a frequency-dependent, complex viscoelastic shear modulus $G^*(f)=G'(f)+jG''(f)$, where $G'(f)$ is the shear storage modulus, $G''(f)$ the loss modulus, and f the frequency. If a mass with mass moment of inertia J and a torsional spring of constant k are attached to one end of the cylinder as shown in figure 1, and the other end of the cylinder is subjected to a harmonically varying torque, then the expression for the angular acceleration response ratio of the top plane of the cylinder to the bottom plane is given by [4,5]

$$A_0=\frac{(\mathrm{Acc})_{\mathrm{TOP}}}{(\mathrm{Acc})_{\mathrm{BOT}}}=\frac{r_t}{r_b}\left[C_1\Omega^*\sin(\Omega^*)+\cos(\Omega^*)\right]^{-1} \quad (1)$$

where

$$C_1=\frac{2J[(f_m/f)^2-1]}{\pi\rho h(b^4-a^4)} \quad (2)$$

$$\Omega^*=x-jy$$

$$f_m=\frac{1}{2\pi}\sqrt{\frac{k}{J}}$$

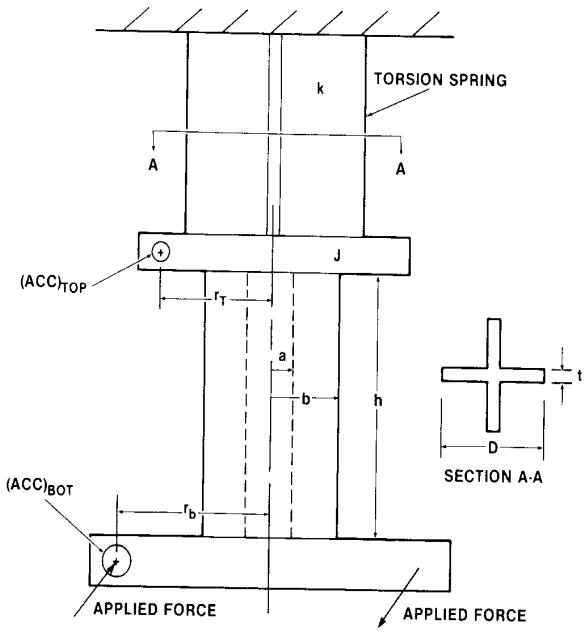

Figure 1—Geometric description of torsion specimen and attached spring and mass.

$$x = 2\pi \cos(\theta/2) \sqrt{\frac{\rho f^2 h^2}{p}}$$

$$y = 2\pi \sin(\theta/2) \sqrt{\frac{\rho f^2 h^2}{p}} \quad (3)$$

$$p = [G'^2 + G''^2]^{1/2}$$

$$\theta = \tan^{-1}(G''/G') \quad (4)$$

and ρ is the density of the cylinder, h its length, b its outer radius, a its inner radius, and G''/G' the loss tangent. The quantity f_m is the natural frequency of the attached spring-mass system with the cylindrical specimen removed. The quantity r_t is the distance from the center of the axis of the cylinder to the center of the top accelerometer, and r_b is the distance from the axis to the point of application of the applied force, which coincides with the location of the bottom accelerometer.

Substituting eq (3) into eq (1) yields

$$A_0 = R e^{j\phi} \quad (5)$$

where

$$R = \frac{r_t}{r_b}(A^2 + B^2)^{-1/2}$$

$$\phi = \tan^{-1}(B/A) \quad (6)$$

and

$$A = [C_1 x \sin(x) + \cos(x)]\cosh(y) - C_1 y \cos(x)\sinh(y)$$

$$B = [C_1 x \cos(x) - \sin(x)]\sinh(y) + C_1 y \sin(x)\cosh(y). \quad (7)$$

Thus, if R and ϕ are the measured amplitude ratio and phase angle, respectively, and all the physical and geometric parameters of the specimen are determined by other means, then G' and G'' can be found using eqs (6) and (7). However, because of the complexity of these equations, G' and G'' cannot be solved for explicity. The numerical procedure used to obtain these quantities is described in Appendix I.

As the excitation frequency approaches zero and $f \ll f_m$ eq (1) becomes

$$A_0 = \left(\frac{r_t}{r_b}\right)\left[1 + \frac{C_0}{G}\right]^{-1} \quad (8)$$

where

$$C_0 = \left(\frac{8\pi h}{b^4 - a^4}\right) J f_m^2 \quad (9)$$

and G is a nominal value for p. The range of values for C_0, in N/m^2, for the experimental setup is approximately $2.5 \times 10^5 \leqslant C_0 \leqslant 2 \times 10^8$. Thus for materials with a shear modulus of 3×10^7 N/m^2, A_0 will vary from a value slightly less than r_t/r_b to a value of approximately $(r_t/r_b)/8$.

Design Considerations

1. General Requirements

The general requirements are that 1.) the specimens can range in size to approximately 15 cm in length and 9 cm in diameter; 2.) the shear moduli can be as low as 3×10^6 N/m^2; and 3.) the method provides the shear modulus over a broad frequency range from 80 to 550 Hz and temperature range from $-20°$ to 80 °C.

2. Temperature Considerations

The temperature requirements place a limit on the overall size of the test fixture, for it has to fit into a temperature chamber of reasonable size. It also has to weigh a modest amount so that one could place it into a chamber without the chamber requiring additional

structural support. Lastly, in order to operate the vibration exciters over the temperature range, the exciters have to be air cooled/heated with room temperature air (20 °C) so that the springs that sustain the exciter's moving element retain their desired properties.

The temperature of the specimen is determined from the placement of a thermocouple on the specimen's surface and is read by a digital output device with an accuracy of ±1 °C.

3. Fixture

According to the theory used to determine the shear modulus from the experimentally determined data, the specimen should be subjected to torsional motion only, with no bending of the specimen. In addition, the fixture itself must be free from structural resonances over a broad frequency range and for test samples of varying length and diameter. The design chosen was a combination of certain features of previous works [4,5] and is shown in figure 2.

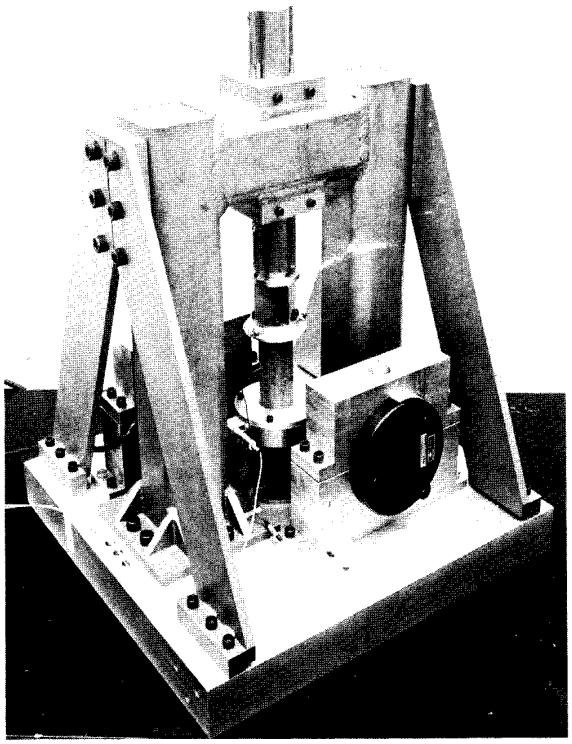

Figure 2—Forced torsional vibration apparatus.

To minimize bending the top and bottom torsional springs have an "x" cross-section, which is very stiff in bending compared to its twisting resistance. To show this consider a single force F acting on the spring through a moment arm about the center of the spring of radius r_b. The displacement due to bending, s_B, is

$$s_B = \frac{1}{3}\frac{FL^3}{EI}$$

and that due to rotation

$$s_T = \frac{Fr_b^2 L}{KG}$$

where G and E are the shear and tensile moduli of the spring, respectively, L is its length and I and K are the moment of inertia and the torsion constant of the cross-section, respectively. The accelerations of the spring are proportional to these displacements. Thus a good measure of their relative resistance to this unbalanced torque is their ratio. Hence,

$$\frac{s_B}{s_T} = \frac{1}{6(1+\upsilon)}\left(\frac{L}{r_b}\right)^2 \frac{K}{I}$$

where υ is Poisson's ratio. For the "x" cross-section shown in figure 1,

$$K \cong \frac{2}{3}Dt^3$$

$$I \cong \frac{tD^3}{12}. \tag{10}$$

Therefore,

$$\frac{s_B}{s_T} = \left(\frac{L}{r_b}\right)^2 \left(\frac{t}{D}\right)^2 \tag{11}$$

The bottom spring has the following dimensions: $L = 8.26$ cm, $r_b = 7.46$ cm, $t = 0.32$ cm, and $D = 10.16$ cm. Using these values in eq (11) yields that $s_B/s_T \cong 0.001$. Thus, the bending displacements can be expected to be on the order of a thousand times less than the desired torsionally induced displacements. In the actual system two dynamic exciters are used, which eliminates most of the unbalanced force. The output force of the shakers, however, is not controlled, and it is assumed that the same input voltage to both exciters yields approximately the same output force. However, because of this great difference in stiffnesses, any small imbalance does not strongly couple to the system. For the top spring the parameters in eq (10) are: $L \cong 5.08$ cm, $t = 0.0794$ cm, and $D = 6.99$ cm. Equation (10) now yields $s_B/s_T \cong 0.0002$.

The experimental confirmation of the excitation portion of the fixture's resistance to bending is shown in figure 3. The input signal to the shakers was broadband random noise. A commercial digital frequency analyzer was used to obtain the time-averaged transfer function of the input voltage to the shakers to the voltage from the bottom accelerometer. The result is shown in figure 3. The absence of any resonance peaks until approximately 680 Hz, except the one directly related to the first torsional resonance of spring-mass system, can be seen. This indicates that the useful frequency range of the fixture is as high as approximately 550 Hz. The torsional natural frequency of the bottom spring mass system is of no consequence in the experiment because the magnitude of the input acceleration is kept relatively constant over the entire test frequency range.

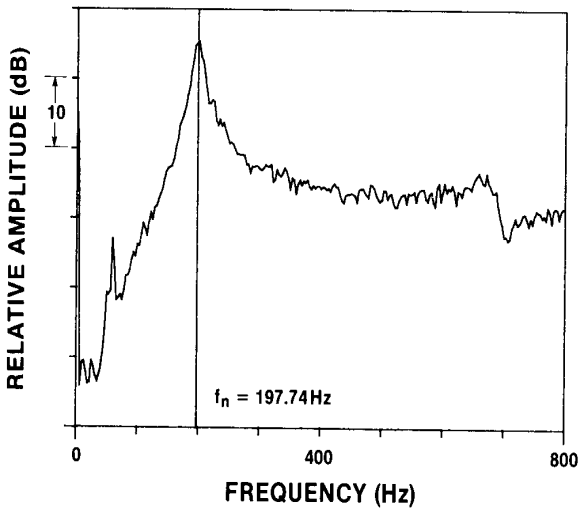

Figure 3—Transfer function of bottom torsional spring and attached mass.

4. Determination of J and f_m

The top end of the top torsion spring is bolted to a movable solid steel cylinder as shown in figure 2. According to the theory developed previously, this connection must be rigid compared to the torsion spring itself. The ratio of the torsional rigidity of the solid cylinder, K_c, to that of the torsion spring, K (given by eq (10)), is

$$\frac{K_c}{K}=\frac{3\pi}{64}\left(\frac{D}{t}\right)^3$$

Substituting in the appropriate dimensional values for the fixture shown in figure 2 yields $K_c/K\cong 10^5$. Thus, the assumption of rigidity is a good one.

Another important consideration is the range of values for J, the mass moment of inertia of the attached mass. For a given natural frequency of this system the specimen, when connected to J, must be able to influence both the value of f_m and, more importantly, its damping. An indication of the magnitude of the parameters that influence these properties can be approximately determined by assuming that the vibrating system consists of the inertia J connected to two springs; one is the "x" cross-section torsion spring already discussed and the other is the spring formed by the torsional resistance of the specimen, assuming that its internal damping can be ignored in this portion of the analysis. The natural frequency of this new system, f_m', is then given by

$$f_m'=f_m[1+C_2]^{1/2} \tag{12}$$

where f_m is given by eq (3) and

$$C_2=\frac{\pi}{2}\left(\frac{G}{h}\right)\frac{(b^4-a^4)}{(2\pi f_m)^2}\left(\frac{1}{J}\right) \tag{13}$$

It is seen that in order for C_2 to be greater than one, the combination of h, f_m, and J must be chosen carefully for a given material. Unfortunately the class of materials that is to be tested is very weak in torsion; typically these materials have a shear modulus of 4 to 15×10^6 N/m^2. Consequently the design requires that J, h, and f_m be as small as possible. There are, of course, some physical limitations in just how small J can be made. In the apparatus shown in figure 2, $J=1.8972$ kg$-$cm^2. The computational procedure to obtain J is given in Appendix II.

Whereas J was computed, the natural frequency of the attached spring/mass system, f_m, without the test specimen attached was determined experimentally by using a digital frequency analyzer in its transfer function mode. The excitation was applied with a hammer to one of the "ears" (see figs. 2 and A-2) of the top mass. The noncontacting end of the hammer had an accelerometer mounted to it. The resulting motion of the spring/mass was recorded by the accelerometer mounted on one of the "ears." Using the zoom capability of the analyzer, f_m was determined to within ±0.25 Hz, which, for natural frequencies $f_m>100$ Hz results in an uncertainty of 0.25% or less. The results for two torsion springs, one with $t=0.7938$ mm and the other $t=1.588$ mm (see fig. 1) and for two thickness of the accelerometer mounting disk (see fig. A-2) are summarized in table 1. From the

Table 1. Values of f_m for four combinations of springs and inertias (J).

	f_m(Hz)	
Spring flange thickness (mm)	$J=1.8972$ kg−cm^2 ($h_A=6.35$ mm)	$J=2.3652$ kg−cm^2 ($h_A=12.75$ mm)
0.7938	100.75	89.00
1.588	283.00	255.00

discussion in the preceding paragraph it is seen that for the weaker class of materials the spring/mass combinations resulting in the lower set of f_m should be used.

5. Specimen Mounting

In order to mount the specimen concentrically with respect to the top and bottom springs and to eliminate any pre-twist of the specimen, the technique employed used two discs, one 12.3 cm in diameter and attached to the bottom "ears" and the other 6.9 cm in diameter and attached to the top "ears" (and included in the calculation of J), each having on one of its faces a concentric raised disk 1.5 mm high and 12.7 mm in diameter. The disks are mounted on their respective bell cranks with the raised disks facing each other. Prior to mounting the cylindrical specimen, the specimen is placed in a lathe to have each of its end planes turned smooth and perpendicular to its axis. In addition, a concentric cylindrical depression is turned on each of the end planes that is 1.59 mm deep and 12.7 mm in diameter. Epoxy is applied to each end plane of the cylindrical specimen and the specimen is placed onto the bottom disk. The top spring mass assembly is then lowered onto the top of the specimen and the epoxy is allowed to cure.

Instrumentation

The computer controlled instrumentation system used to measure the accelerometers' amplitude ratio and phase angle is shown in figure 4. The electrodynamic vibration exciters are connected in parallel and receive their input voltage from an amplifier with the capacity to provide 15A rms into 1 ohm. The input to the amplifier is connected to an oscillator. The exciters themselves have an impedance of approximately 2 ohms and require 5A rms to obtain their rated output force. The oscillator's output voltage amplitude and frequency are under computer control.

The accelerometers have a sensitivity of nominally 10 mV/g and have a unity gain preamplifier built into them. The output signals from the accelerometers are then amplified 30 dB and passed through two 2 Hz bandwidth tracking filters. The tracking frequency is provided by a second output signal from the oscillator which remains constant at 1 V. This 1 V signal is amplified to meet the tracking filter's requirement of 3.5 V. The 30 dB gain given to each accelerometer signal provides better use of the dynamic range of the tracking filters and uses the digital phasemeter in a voltage range in which its accuracy is better, namely, at levels above 50 mV rms. To maintain control over the voltage levels throughout the electronic measuring system, the output voltage of the oscillator is continuously adjusted so that the output voltage of the bottom accelerometer remains approximately constant at 2.5 mV rms over the entire test frequency range.

The signals from the output of the tracking filters are sent directly to the digital phasemeter and the digital voltmeter, both of which are under computer control. However, the signals to the voltmeter are read sequentially with the aid of a computer controlled switching setup. The phasemeter has an autocalibration feature which is employed every sixth measurement to ensure that the phase measurements are as precise as possible. The digital voltmeter is used in its autoranging mode, since the output voltage for the upper accelerometer differs widely over the frequency range.

The purpose for the attenuator (labeled ATTN) is discussed in detail subsequently.

To accurately measure the acceleration ratio of the top accelerometer to the bottom one and the phase angle between them, one must remove from the measured data the influences of any electronics inserted between the electrical signal at the output of the accelerometers and the recording instruments: the digital voltmeter and the digital phasemeter. The ultimate accuracy of the measurement depends, of course, on the accuracy of the voltmeter and the phasemeter. In this experiment the voltmeter has an accuracy of approximately ± 0.2 dB for rms voltage above 100 mV and ± 0.3 dB for voltages less than 100 mV and greater than 100 μV over the frequency range 1 to 2000 Hz. The phasemeter has an accuracy of $\pm 0.1°$ for rms voltages greater than 50 mV and $\pm 0.2°$ for rms voltages as low as 1 mV from 50 Hz to 50 KHz.

The effects of the intervening electronics are removed in the following manner. Consider the simplified equipment diagram given in figure 5. Let $H_j(f)$ be the transfer function of the accelerometer's built-in impedance converters, H_{Gj} the transfer function of the 30 dB fixed gain amplifiers, and H_{Fj} the transfer function of the tracking filter, where $j=1$ refers to the bottom accelerometer channel and $j=2$ to the top channel. The true

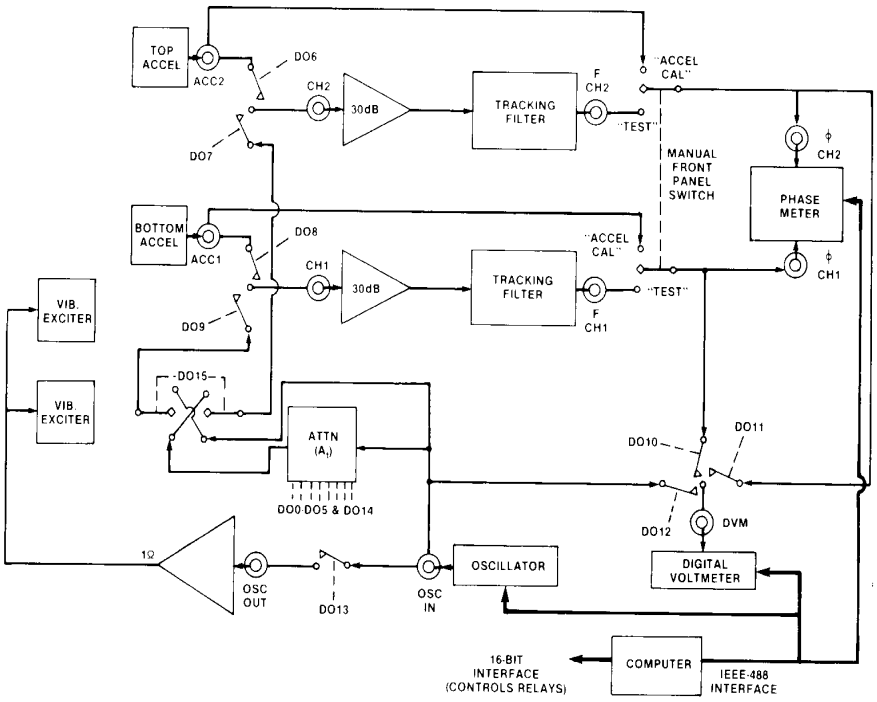

Figure 4—Schematic of complete instrumentation system.

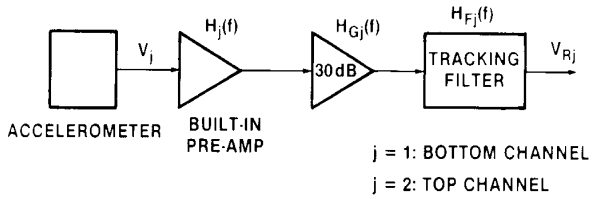

Figure 5—Simplified version of a portion of the instrumentation system.

output signals from the accelerometers, V_j, are related to the signals appearing at the inputs to the digital voltmeter and phasemeter, V_{Rj}, as follows:

$$V_{Rj}=V_j H_j H_{Gj} H_{Fj}, j=1,2. \tag{14}$$

Solving eq (14) for the acceleration ratio $A_0=V_2/V_1$ yields

$$\frac{V_2}{V_1}=\left(\frac{V_{R2}}{V_{R1}}\right)\left(\frac{1}{C}\right) \tag{15}$$

where C is a complex quantity given by

$$C=\left(\frac{H_2}{H_1}\right)\left(\frac{H_{G2}H_{F2}}{H_{G1}H_{F1}}\right). \tag{16}$$

Thus, the amplitude ratio and phase angle are, respectively,

$$\left|\frac{V_2}{V_1}\right|=\left|\frac{V_{R2}}{V_{R1}}\right|\left|\frac{1}{C}\right|$$

$$\phi_{21}=\phi_{R21}-\phi_c \tag{17}$$

where $|V_{R2}/V_{R1}|$ is the ratio of the values read from the digital voltmeter and ϕ_{R21} is the value read from the digital phasemeter. The quantity $|C^{-1}|$ is the correction that must be isolated and measured in order to remove the influence of the electronic components on the amplitude measurement and ϕ_c is the quantity that must be isolated and measured to remove the influence on the phase angle measurement.

To remove the effects of C at a given temperature, we proceed by first removing H_{Gj} and H_{Fj} from the measurement chain and then performing a back-to-back calibration of the two accelerometers. Thus, $V_2=V_1 e^{j\pi}$ (since one accelerometer is upside down with respect to the other) and

$$\left|\frac{H_2}{H_1}\right|=\left|\frac{V_{R2}}{V_{R1}}\right|_{BB}$$

$$\phi_{21}=\phi_{BB}+\pi \tag{18}$$

where $|V_{R2}/V_{R1}|$ is determined directly from the reading of the digital voltmeter and ϕ_{BB} directly from the

digital phasemeter. A picture of the back-to-back calibration fixture is shown in figure 6.

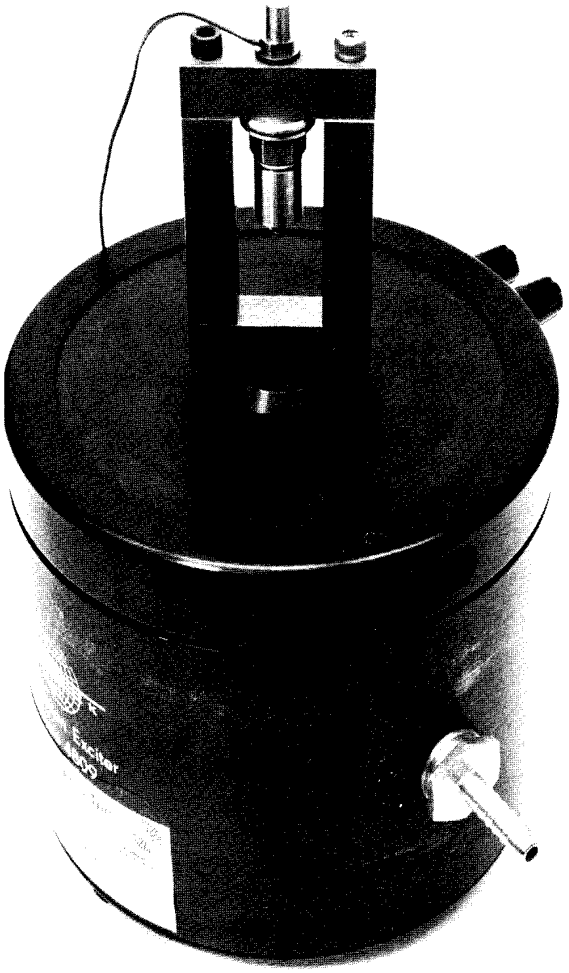

Figure 6 – Back-to-back calibration fixture.

We now disconnect the accelerometers from the measurement chain and replace them by two signals at the same frequency that differ only in amplitude and not phase. Thus $V_1H_1=V_I$ and $V_2H_2=A_tV_I$ where V_I is the amplitude of the input voltage to both channels and $0<A_t<1$. The attenuation A_t is introduced because of the high degree of amplitude and phase nonlinearity of the tracking filters. The introduction of the attenuator allows the input signals to each channel to be approximately equal (to within ±2.5 dB) to each accelerometer's output signal. In the actual test procedure the attenuation A_t can be introduced to either channel depending on whether or not the accelerometer's output signal ratio is greater than or less than 1. If the A_t is switched, then A_t is simply replaced by $1/A_t$ in the subsequent results. Equation (17) then yields

$$\left|\frac{H_{G2}H_{I2}}{H_{G1}H_{F1}}\right| = A_t \left|\frac{V_{R2}}{V_{R1}}\right|_I$$

$$\phi_{21}=\phi_I \tag{19}$$

where $|V_{R2}/V_{R1}|_I$ is determined directly from the readings of the digital voltmeter and ϕ_I directly from the digital phasemeter. Using eqs (18) and (19) yields the desired result

$$\left|\frac{V_2}{V_1}\right| = \left|\frac{V_{R2}}{V_{R1}}\right|\left[A_t\left|\frac{V_{R2}}{V_{R1}}\right|_{BB}\left|\frac{V_{R2}}{V_{R1}}\right|_I\right]^{-1}$$

$$\phi_{21}=\phi_{R21}-\phi_{BB}-\pi-\phi_I \tag{20}$$

The test procedures used to determine the quantities in eq (20) are done under computer control using a set of 16 relays.

In the actual testing of the accelerometer's back-to-back response it was found that at a given temperature it could be assumed that the accelerometers' relative amplitudes are constant over the frequency range of interest and that the phase difference was essentially zero. In other words $|V_{R2}/V_{R1}|_{BB}=C_3$, a constant and $\phi_{BB}=0$ in eq (18). The constant C_3 is determined at each temperature at a nominal frequency of 200 Hz.

The errors associated with the measurement of the amplitude ratio and phase angle cannot be easily related to the resulting errors in the determination of the shear modulus because of the highly nonlinear nature of eqs (5) to (7). Consequently, to get an estimate of the accuracy of the numerically evaluated G' and G'', the following procedure is used. Equation (1) is evaluated over a frequency range for an assumed value of G' and G''. This results in a set of amplitude ratios (A_0) and phase angles (ϕ) as a function of frequency. The set of A_0 and ϕ is then altered by the accuracy of the digital voltmeter and phasemeter, and the inverse problem is considered. Thus, at a given frequency we change the amplitude ratios by up to ±0.2 dB and the phase angle by up to ±0.3° and solve eq (11) for G' and G''. This procedure was used for $J=1.9$ kg–cm^2, $f_m=100$ Hz, $\rho=1000$ kg/m^3, $G'=20\times10^6$ N/m^2, $G''/G'=0.4$, $h=10$ cm, $b=5$ cm, and $a=0$. It was found that the percentage errors in G' and G''/G' are small (<5%) and asymmetrical with respect to the errors in the amplitude and phase at frequencies away from f_m and large and unequal at frequencies at or near f_m, with the largest errors occurring in the loss tangent (±15%).

Another inaccuracy in the determination of the values for G' and G'' are errors due to the calculation of J and the determination of f_m in eq (2). Using a procedure similar to that done previously showed that the effects

of J and f_m was less than $\pm 3\%$ except at $f = 100$ Hz where it was $\pm 6\%$. There are no effects of the errors in J and f_m on the ratio G''/G'.

Results

The apparatus and computer controlled test procedure were used to determine the complex shear modulus of an inhomogeneous polyurethane material with 4% of its volume containing air bubbles. The sample was 5.08 cm in diameter and its original height was 10.16 cm. Several different combinations of measurements were made to get an estimate of the variability of the complex shear modulus values as a function of slight changes in specimen temperature, choice of f_m, and the height of the specimen. To determine the latter effect the original 10.16-cm-high specimen was cut into two pieces, one 4.8 cm high and the other 4.9 cm high. The results are tabulated in tables 2 and 3.

Using both tables and comparing the results of the data in column 1 with those in column 2, those of column 3 with those of 4, 5 with 6, and those of column 7 with those of 8, it is seen that the repeatability of the data is excellent—typically better than 1% for both the storage modulus and the loss tangent. Comparison of columns 3 – 6 of both tables indicates that the effect of a choice of f_m also yields a repeatability of better than 1% for the storage modulus and 8% for the loss tangent. The large variation in the loss tangent is consistent with the results found from the error analysis described in the previous section.

In comparing columns 1 and 2 with columns 3 and 4 and with columns 7 and 8, it is seen that the change in length of the specimen yields results that are within 4% of each other. This small deviation is probably due to the unequal distribution of the air bubbles within the material.

Comparing columns 7 and 8 with column 9 shows the change in values of the moduli due to the change in the test site. Although the loss tangent seemed to remain unchanged, the shear storage modulus inexplicably decreased by about 7%.

The apparatus and test method produce data that are self-consistent. In addition, when the results are compared to values obtained previously from other tests at much higher frequencies, but on the same sample, these values are what are expected.

The 4.8-cm-high specimen was tested over a range of temperatures from -10 °C to 40 °C with $f_m = 100.8$ Hz. The results are shown in figures 7 and 8 where they

Table 2. Variability of the storage modulus (G') as a function of several test parameters.

	1	2	3	4	5	6	7	8	9
Length (cm)	10.16	10.16	4.8	4.8	4.8	4.8	4.9	4.9	4.9
f_m (Hz)	100.8	100.8	100.8	100.8	89.0	89.0	100.8	100.8	100.8
Temperature (°C)	24.0	24.2	21.2	21.9	23.2	23.2	21.1	22.3	22.6
Date	1 Sept 82	1 Sept 82	7 Sept 82	7 Sept 82	7 Sept 82	7 Sept 82	3 Sept 82	3 Sept 82	15 Sept 82
Time	11:39	12:18	9:36	10:27	14:52	15:49	9:29	11:09	15:11
Frequency (Hz)					G' (N/m^2)				
100			14.28	13.57	15.66	15.52			12.87
110	14.51	14.45	14.13	14.06	15.33	15.27	18.46	18.32	12.97
120	14.58	14.53	15.18	15.43	14.84	14.84	16.47	16.48	13.88
130	14.36	14.33	14.51	14.43	14.92	14.91	15.45	15.39	13.38
140	14.38	14.56	14.82	14.66	15.13	15.14	15.49	15.33	13.55
150	14.65	14.70	15.11	14.97	15.12	15.13	15.70	15.48	14.42
160	14.93	14.86	15.09	14.91	15.12	15.12	15.62	15.41	14.54
170	15.32	15.25	14.93	14.75	15.22	15.22	15.48	15.30	14.55
180	15.27	15.11	14.94	14.72	15.34	15.35	15.52	15.30	14.36
190	15.63	15.57	15.09	14.88	15.46	15.46	15.66	15.49	14.47
200	15.66	15.53	15.11	15.01	15.55	15.57	15.74	15.61	14.54
210			15.30	15.20	15.82	15.82	15.92	15.84	14.64
220			15.61	15.52	15.94	15.94	16.05	15.96	14.92
230			16.26	16.18	16.43	16.45	16.30	16.17	15.27
240			16.54	16.47	16.72	16.70	16.43	16.31	15.18
250			16.54	16.42	16.96	16.99	16.39	16.27	15.33
260			16.77	16.64	17.39	17.40	16.63	16.51	15.47
Test Site:				NBS					NSRDC

Table 3. Variability of the loss tangent (G''/G') as function of several test parameters.

	1	2	3	4	5	6	7	8	9
Length (cm)	10.16	10.16	4.8	4.8	4.8	4.8	4.9	4.9	4.9
f_m (Hz)	100.8	100.8	100.8	100.8	89.0	89.0	100.8	100.8	100.8
Temperature (°C)	24.0	24.2	21.2	21.9	23.2	23.2	21.1	22.3	22.6
Date	1 Sept 82	1 Sept 82	7 Sept 82	7 Sept 82	7 Sept 82	7 Sept 82	3 Sept 82	3 Sept 82	15 Sept 82
Time	11:39	12:18	9:36	10:27	14:52	15:49	9:29	11:09	15:11
Frequency (Hz)					G''/G'				
100			.269	.173	.125	.140			.703
110	.224	.222	.360	.310	.184	.180	.238	.203	.406
120	.229	.227	.302	.249	.200	.204	.275	.269	.352
130	.230	.226	.250	.249	.210	.211	.231	.237	.320
140	.260	.287	.252	.250	.220	.220	.240	.238	.259
150	.255	.263	.254	.252	.218	.218	.247	.246	.226
160	.255	.256	.256	.253	.220	.220	.254	.252	.217
170	.241	.244	.253	.252	.210	.210	.246	.243	.222
180	.253	.223	.247	.249	.211	.211	.235	.230	.237
190	.224	.228	.260	.256	.215	.215	.237	.232	.240
200	.245	.248	.275	.271	.220	.218	.243	.241	.245
210			.287	.287	.232	.231	.241	.241	.249
220			.303	.302	.245	.245	.243	.240	.246
230			.291	.287	.245	.244	.242	.243	.249
240			.278	.275	.241	243	.247	.248	.254
250			.280	.281	.238	.236	.251	.249	.253
260			.279	.278	.228	.226	.250	.250	.255
Test Site:				NBS					NSRDC

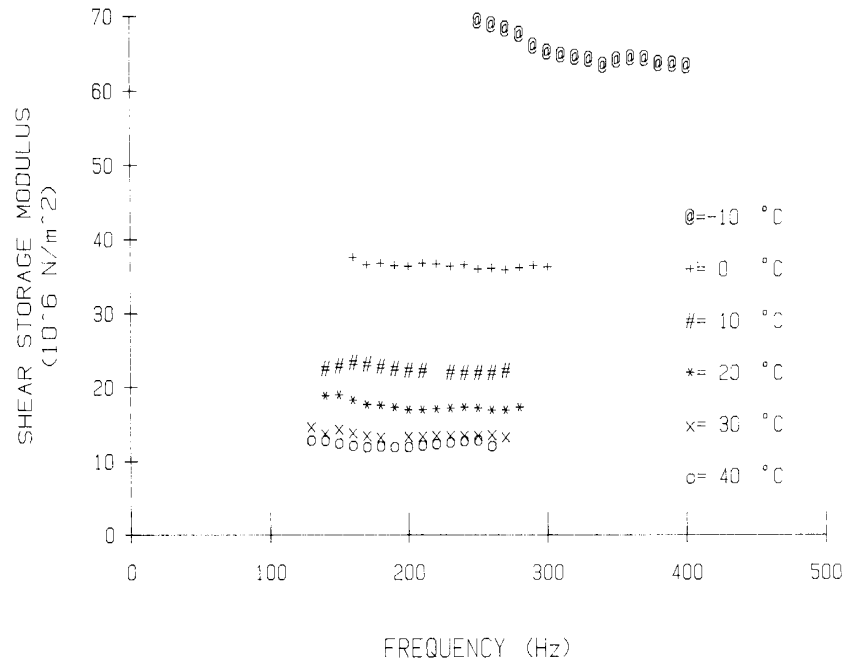

Figure 7—Shear storage modulus of polyurethane with 4% air as a function of frequency and temperature.

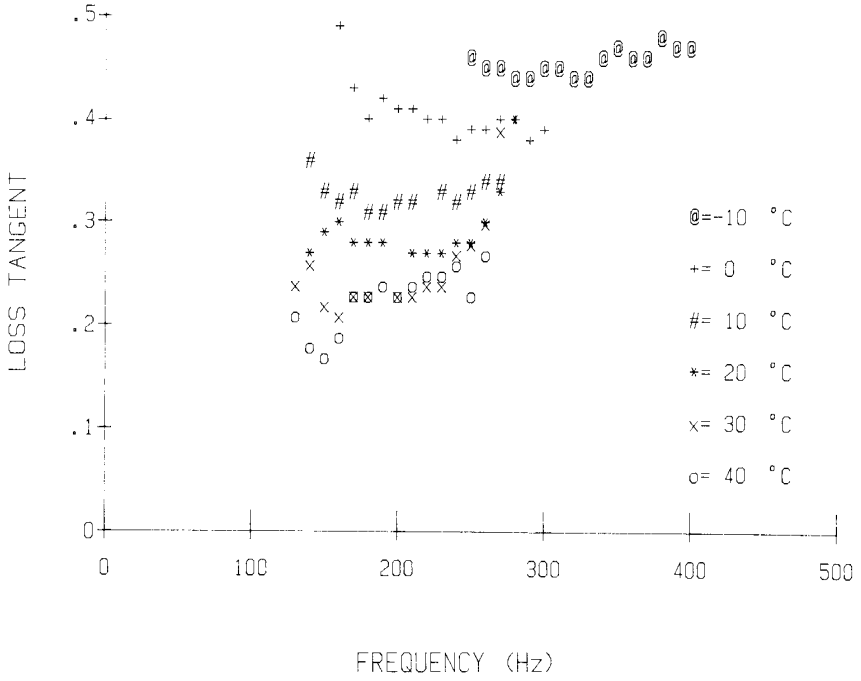

Figure 8—Loss tangent of polyurethane with 4% air as a function of frequency and temperature.

exhibit the desired properties of high loss tangent at decreasing temperatures and of being relatively frequency independent. Unfortunately, from a rheological point of view this material does not exhibit the property of time-temperature equivalence and therefore cannot be reduced to a composite master curve that would effectively produce shear moduli data at a given temperature over a much greater frequency range than shown.

The assistance of William Penzes, for his design and construction of the switching network, 30 dB amplifiers, and various power supplies and connectors, is greatfully acknowledged.

R. Reitz of the U.S. Naval Research and Development Center obtained the data presented in figures 7 and 8.

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Appendix I

Marquardt's Minimization Procedure

The values of G' and G'' are obtained from eqs (6) and (7) using Marquardt's method [6, 7]. The method will be outlined below and the specific functions for our particular case will be given.

The Marquardt procedure is an efficient means of minimizing

$$S(\mathbf{x})=\sum_{i=1}^{m}[\mathbf{f}_i(\mathbf{x})]^2=\mathbf{f}^T\mathbf{f} \tag{I-1}$$

where

$$f_i(\mathbf{x})=g_i(\mathbf{x})-g_i' \tag{I-2}$$

and $g_i(\mathbf{x})$ are the m (nonlinear) functions of the parameters $\mathbf{x}(x_1, x_2, .. x_n)$ and g_i' are the measured values. Equation (I-2) states that we are minimizing the sum of the squares of the deviation of the data from the functions used to fit these data. In our case, $m=2$ and $n=2$. The Marquardt procedure says that a good next guess for the value of the parameter $\mathbf{x}$, denoted $\mathbf{x}+\mathbf{q}$, can be determined from an iterative solution to

$$(\mathbf{J}^T\mathbf{J}+\lambda\text{Dia}[\mathbf{J}^T\mathbf{J}])\mathbf{q}=-\mathbf{J}^T\mathbf{f} \tag{I-3}$$

where $\mathbf{J}$ is the Jacobian matrix whose elements are defined as

$$J_{ij}=\frac{\partial}{\partial x_j}f_i(\mathbf{x}). \tag{I-4}$$

The superscript T denotes the transpose of the matrix and Dia [...] denotes that the matrix has all zero elements except along its diagonal. The left hand side of eq (I-4) must be positive definite and, therefore, λ must always be chosen so that this side keeps its positive definiteness. The positive-definiteness is determined in the solution to eq (I-3) by using the Choleski decomposition of the matrix on the left hand side and checking to see that each diagonal term of the decomposed matrix is greater than zero, which indicates positive-definiteness. If they are not all greater than zero, the value of λ is increased by a factor of ten.

The iterative solution itself is straightforward. Starting with a value of $\lambda=0.1$, λ is reduced by a factor of 2.5 before each step in the solution if the preceding solution for $\mathbf{q}$ has given

$$S(\mathbf{x}+\mathbf{q})<S(\mathbf{x}).$$

If

$$S(\mathbf{x}+\mathbf{q})\geqslant S(\mathbf{x})$$

then λ is increased by a factor of 10. The process is repeated until certain convergence criteria have been satisfied.

For our particular case we have from eq (6) that $x_1=G'$, $x_2=G''$, $g_1=D'$, and $g_2=\phi$, where, for convenience, we defined $D'=(r_b/r_t)R$. Since D' and ϕ are functions of x and y, which in turn are functions of G'' and G', it is easiest to use the chain rule for partial differentiation to obtain the four elements of the Jacobian matrix. Thus

$$J_{11}=\frac{\partial D'}{\partial G'}=\frac{\partial D'}{\partial x}\frac{\partial x}{\partial G'}+\frac{\partial D'}{\partial y}\frac{\partial y}{\partial G'}$$

$$J_{12}=\frac{\partial D'}{\partial G''}=\frac{\partial \mathrm{D}'}{\partial x}\frac{\partial x}{\partial G''}+\frac{\partial D'}{\partial y}\frac{\partial y}{\partial G''}$$

$$J_{21}=\frac{\partial\phi}{\partial G'}=\frac{\partial\phi}{\partial x}\frac{\partial x}{\partial G'}+\frac{\partial\phi}{\partial y}\frac{\partial y}{\partial G'}$$

$$J_{22}=\frac{\partial\phi}{\partial G''}=\frac{\partial\phi}{\partial x}\frac{\partial x}{\partial G''}+\frac{\partial\phi}{\partial y}\frac{\partial y}{\partial G''}$$

where

$$\frac{\partial D'}{\partial x}=-[A^2+B^2]^{-3/2}\left[A\frac{\partial A}{\partial X}+B\frac{\partial B}{\partial x}\right]$$

$$\frac{\partial D'}{\partial y}=-[A^2+B^2]^{-3/2}\left[A\frac{\partial A}{\partial y}+B\frac{\partial B}{\partial y}\right]$$

$$\frac{\partial\phi}{\partial x}=[A^2+B^2]^{-1}\left[A\frac{\partial B}{\partial x}-B\frac{\partial A}{\partial x}\right]$$

$$\frac{\partial\phi}{\partial y}=[A^2+B^2]^{-1}\left[A\frac{\partial B}{\partial y}-B\frac{\partial A}{\partial y}\right]$$

A and B are given by eq (7) and their derivatives are

$$\frac{\partial A}{\partial x}=[(C_1-1)\sin(x)+C_1x\cos(x)]\cosh(y)+C_1y\sin(x)\sinh(y)$$

$$\frac{\partial A}{\partial y}=[C_1x\sin(x)+(1-C_1)\cos(x)]\sinh y-\mathrm{C}_1\, y\, \cos(x)\, \cosh\, (y)$$

$$\frac{\partial B}{\partial x}=-\frac{\partial A}{\partial y}$$

$$\frac{\partial B}{\partial y}=[C_1x\cos(x)+(C_1-1)\sin(x)]\cosh(y)+C_1y\sin(x)\sinh(y).$$

The remaining partial derivatives are obtained from eq (4). Thus,

$$\frac{\partial x}{\partial G'}=-\frac{1}{2p^2}\,[xG'-yG'']$$

$$\frac{\partial x}{\partial G''}=-\frac{1}{2p^2}\,[xG''+y\,G']$$

$$\frac{\partial y}{\partial G'}=\frac{\partial x}{\partial G''}$$

$$\frac{\partial y}{\partial G''}=-\frac{\partial x}{\partial G'}$$

Returning to eq (I-3) we can now write the solution for q_1 and q_2 in terms of the elements of the Choleski decomposed matrix L_{ij} as

$$q_2=v_1/L_{22}$$

$$q_1=(v_1-L_{21}q_2)/L_{11}$$

where

$$v_1 = b_1/L_{11}$$

$$v_2 = (b_2 - L_{21}v_1)/L_{22}$$

$$L_{11} = \sqrt{A_{11}}$$

$$L_{21} = A_{21}/\sqrt{A_{11}}$$

$$L_{22} = A_{22} - A_{21}^2/A_{11}$$

and

$$b_1 = J_{11}f_1 + J_{21}f_2$$

$$b_2 = J_{12}f_1 + J_{22}f_2$$

$$A_{11} = (1+\lambda)\ (J_{11}^2 + J_{21}^2)$$

$$A_{12} = J_{11}J_{12} + J_{22}J_{21}$$

$$A_{22} = (1+\lambda)\ (J_{12}^2 + J_{22}^2)$$

$$A_{21} = A_{21}.$$

When $L_{22} > 0$ the matrix is positive definite.

Appendix II

Computation of the Mass Moment of Inertia J

The total mass moment of inertia, J, is comprised of the following parts: (1) the base of the torsion spring; (2) the accelerometer mounting arm, including the accelerometer and the counter balance; (3) the specimen mounting plate; and (4) the Allen screw heads. Referring to figures A-1 to A-4, the following formulas and numerical values are obtained:

Torsion Spring Base

The mass moment of inertia, J_D, using figure A-1, is

$$J_2 = \frac{1}{2} W_D r_D^2$$

where W_D is the weight of the base and is given by

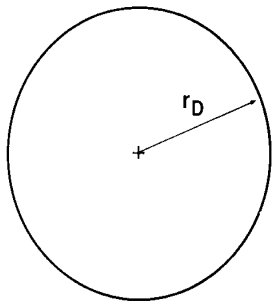
$$W_D = \pi h_D r_D^2 \rho$$

where ρ is the density of the base material. For steel, $W_D = 0.09548$ kg and $J_D = 0.5825$ kg$-$cm^2.

Accelerometer Mounting Arm and Accelerometer

The mass moment of inertia, J_S, using figure A-2 is

$$J_2 = \frac{W_c}{2}(r_0^2 + r_i^2) + 2W_0\left(\frac{L^2}{12} + d_2^2\right)$$



$r_D = 34.93\,mm$

$h_D = 3.18\,mm$

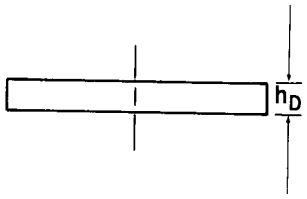
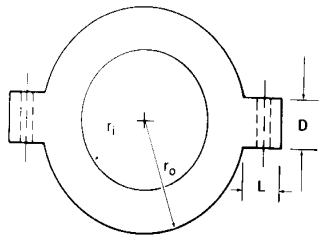


Figure A-1 – Dimensions of torsion spring base.



r_o = 34.93mm
r_i = 22.22mm
r_h = 2.54mm
d_1 = 47.63mm
d_2 = 41.28mm
D = 19.05mm
L = 12.7mm
h_A = 6.35 or 12.70mm

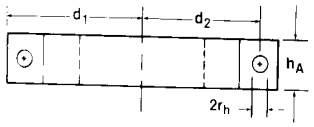


Figure A-2 – Dimensions of attached mass and top accelerometer's mounting position.

where

$$W_c = \rho h_A \pi (r_0^2 - r_i^2)$$

$$W_0 = \rho h_A (LD - \pi r_A^2) + W_{ACC}$$

and W_{ACC} is the weight of the accelerometer (2.5 gm). For aluminum, $W_C = (6.190 \times 10^{-3}) h_A$ kg and $W_0 = (6.013 \times 10^{-4}) h_A + 0.0025$ kg. Then for $h_A = 6.35$ mm, $J_S = 0.4680$ kg – cm^2 and for $h_A = 12.7$ mm, $J_S = 0.9360$ kg – cm^2.

Specimen Mounting Plate

The mass moment of inertia, J_M, using figure A-3, is

$$J_M = \frac{1}{2}(W_t r_t^2 + W_b r_b^2)$$

where

$$W_t = \rho h_t \pi r_t^2$$

and

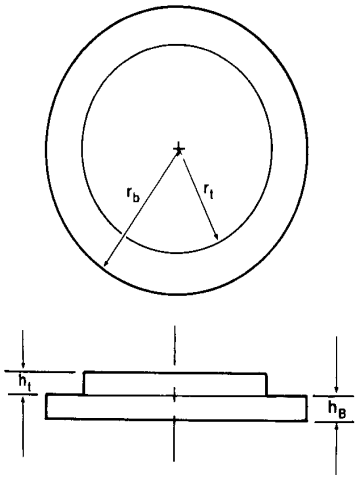
$$W_b = \rho h_b \pi r_b^2.$$

For aluminum, $W_t = 0.03307$ kg and $W_b = 0.05355$ kg. Then $J_M = 0.7308$ kg – cm^2.

Allen Screw Heads

The mass moment of inertia, J_H, using figure A-4, is,

$$J_H = 4\left[W_b\left(\frac{1}{2}r_c^2 + d_3^2\right) + W_t\left(\frac{1}{2}(r_c^2 + r_d^2) + d_3^2\right)\right]$$



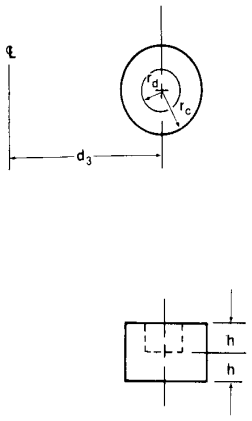
r_b = 44.45mm

r_t = 34.93mm

h_t = 3.18mm

h_B = 3.18mm

Figure A-3 – Dimensions of specimen mounting plate.



	LARGE	SMALL
h	3.18mm	1.98mm
r_d	2.38mm	2.38mm
r_c	4.37mm	3.57mm
d_3	28.58mm	

Figure A-4 – Dimensions of Allen screw heads.

where

$$W_b = \rho h \pi r_c^2$$

and

$$W_t = \rho h\ \pi(r_c^2 - r_d^2).$$

For the large screws, $W_b = 0.00149$ kg and $W_t = 0.00105$ kg. For the small screw, $W_b = 0.000621$ kg and $W_t = 0.000345$ kg. Then, for the large screws $J_H = 0.08408$ kg-cm^2 and for the small screws $J_H = 0.03185$ kg$-$cm^2. The total is $J_H = 0.1159$ kg$-$cm^2.

Total Mass Moment of Inertia

The mass moment of inertia is equal to

$$J = J_D + J_S + J_M + J_H$$

For the two accelerometer mounting plates of thickness h_A we have:

$h_A = 6.35$ mm:	$J = 1.8972$ kg$-$cm^2
$h_A = 12.7$ mm:	$J = 2.3652$ kg$-$cm^2.

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An Ultrasonic Absolute Power Transfer Standard

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In response to increased interest in the use of calibrated sources of ultrasonic energy, we have developed a system comprising components grouped to facilitate the accurate transfer of calibration. Electronic circuitry supplied with and built into each ultrasonic transducer obviates both the use of not-readily-available radio-frequency equipment and the measurement of anything more exotic than dc voltage. Prototype transducers have shown good output at frequenices up to 78 MHz. Units now available to the public can be calibrated at output powers ranging from 5 mW to 500 mW at frequencies between 1 and 20 MHz.

Key words: transfer calibrations; ultrasonic power standards; ultrasonic transducers.

1. Introduction

Among the numerous ways in which ultrasonic transducers might be characterized, [1,2],[1] methods involving total radiated output power are outstanding both for conceptual elegance and for relative ease of implementation. Additional motivation for the use of measurements of total output power to describe the behavior of ultrasonic transducers derives from the needs of such diverse applications as medical ultrasonics and quantitative nondestructive testing. Recent increases in the use of medical ultrasonic procedures have dramatically augmented the importance of dosimetry, and thus of basic power measurements.

A method used for some time at NBS involves the determination of transducer output power from the radiation force, [3]. With our apparatus, the measurement of radiation force depends ultimately on readily-verified knowledge of the transfer characteristics of a magnetic driver. Transfer of the calibration of our radiation force balance to other power-measuring instruments is done using standard source transducers such as those developed at NBS. Given only the very realistic assumption of good long-term transducer stability, levels of ultrasonic power output can be reproduced almost as accurately as measurements of the applied rf voltage can be made and later repeated. In the event that the input voltage and output pressure of a transducer are proportional, use of a coefficient of proportionality for a particular frequency allows the generation of arbitrary power levels. A series of air-backed half-wave resonant quartz standard transducers developed for this purpose and characterized by an appropriate coefficient, the radiation conductance, has proven to be both convenient and useful. Results of extensive international tests of this series of transducers have recently been reported [4]; all quantitative aspects were consistent with expectation.

This report describes a new ultrasonic power calibration system developed as a result of further investigation of the limitations of the previous design, and in response to the needs revealed by consultation with past and potential users of standard ultrasonic sources.

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[1]Figures in brackets indicate literature references at the end of this paper.

2. Distinctive Features of the New System

Several avenues have been available for the transfer of NBS measurements of ultrasonic power. A calibration service featuring either our radiation force apparatus or a calorimeter [2], as appropriate, offers measurements on transducers alone or in tandem with their driving electronics. For the purpose of calibrating systems for ultrasonic power measurements in other laboratories, NBS standard sources are available for loan in consideration of a fee for their recalibration upon return. It is this latter application which is addressed by our new system. The new system reduces and simplifies the effort required of the user. By allowing for operation at several frequencies, the design of the new transducers substantially reduces the amount of equipment required to cover a given frequency span.

Radio-frequency energy for continuous-wave ultrasonics work is usually derived from a signal generator (oscillator or synthesizer) driving a power amplifier. Since the electrical impedance of a typical standard source departs widely from the 50 ohm output impedance of the usual power amplifier, the interests of economic and electrical efficiency dictate the use of an impedance-matching network between power amplifier and transducer. Under most circumstances of operation, the impedance of our new standard source is outside the operating range of matching networks known to be commercially available. Attempts to use matching networks of conventional design to drive the new source result in low overall efficiency (a few percent) and consequent severe overheating of the matching network. These problems are avoided by providing suitable matching networks of customized design with each transducer. Our networks employ a small module interposed between the transducer and connecting cable, and a conventionally-adjustable unit between the connecting cable and power amplifier.

Another problem encountered in the field involves measurement of applied rf voltage. Substantial errors can arise both from circulating currents outside interconnecting cables and within nearby metallic apparatus, and from the use of insufficiently short cabling between transducer and voltmeter. Circulating currents cannot easily be anticipated nor controlled, while the physical configuration in many applications involving submerged use of a standard source precludes the use of short cabling. These onerous contingencies are circumvented with our new system by the inclusion of voltage-measuring circuitry inside the transducer itself. A proportional dc signal is carried from the transducer in the same conductor carrying rf excitation to the transducer; an external splitter inserted anywhere between the transducer and the matching network allows connection of a dc voltmeter. This arrangement is shown in figure 1. In this application only the precision and stability of the metering circuit are important; accuracy and linearity are of secondary importance as design criteria. Component values are chosen to optimize the precision attainable with a particular dc voltmeter range over the intended ultrasonic power range. Typical values for isolation resistors R_1 and R_2 are 10 megohms when a dc voltmeter of 10 megohm input resistance is used. Divider capacitors C_3 and C_4 typically range from 10 pF to 100 pF. A 5000 pF capacitor serves as bypass capacitor C_2. Silvered mica capacitors and metallized film resistors are used throughout. In addition to eliminating the possibility of errors inherent to the use of external rf-measuring equipment, the use of built-in metering allows the transfer of rf voltage measurements with improved accuracy; the same device can be used by both NBS and the user to reproduce predetermined voltage

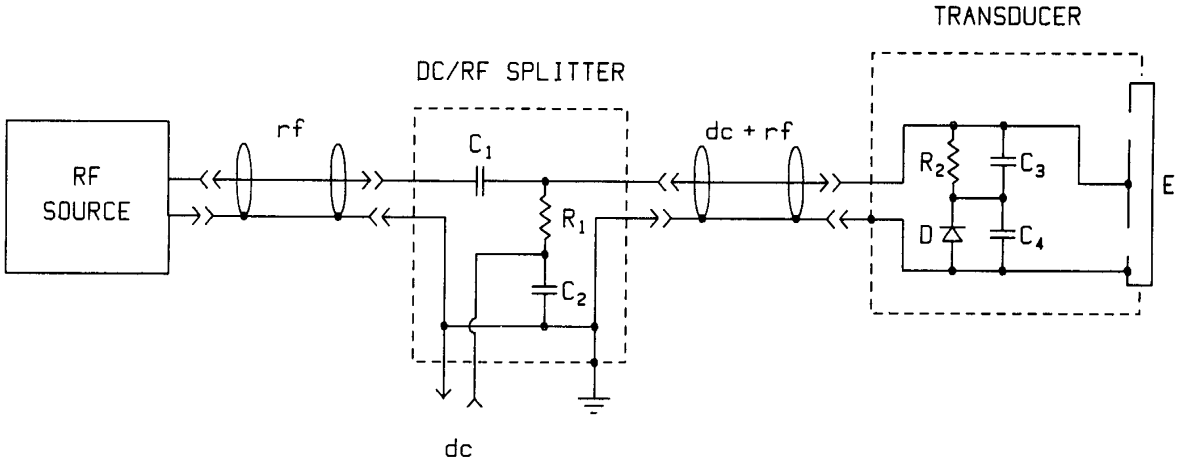

Figure 1—Interconnection of system components.

levels with accuracy limited only by the dc voltmeters used. This procedure allows the transfer of NBS measurements of output power to be effected directly, without use of a derived radiation conductance. It is expected that use of this direct procedure will offer a significant improvement in the overall accuracy of calibration transfer. (The present estimate of uncertainty for measurements of radiation conductance is 3% to 8%, increasing with frequency.)

3. Distinctive Features of the New Transducer

The configuration chosen for the transducer unit (fig. 2) shares with its predecessors from NBS the use of a 2.54-cm-diameter coaxially plated piezoelectric element. In the interest of durability, the metal-plastic composite case material used earlier has been replaced by stainless steel. The overall length of the unit has been reduced to less than 12 cm including the electrical connector. The possibility of unwanted electrical coupling between the transducer and its surroundings (e.g., metallic mounting fixtures) has been diminished by the incorporation of a feature which avoids the flow of current in the transducer housing: three isolated internal wires connect the inner surface of the "wrap-around" ground electrode to the outer shell of the BNC connector. Electrical isolation of the crystal element is preserved by the use of a formed-in-place silicone rubber support for the element. The use of compliant mounting is intended to foster stability of performance by minimizing coupling of unwanted possible modes of ultrasonic vibration from the crystal element to the housing, loading of the crystal element by the mount, and the application of static stresses to the crystal element. Overall control of the mechanical environment of the transducer element is much improved in comparison to that of earlier designs. Because of the paucity of suitable waterproof connectors, a standard BNC connector is used and it is left to the user to provide the waterproofing necessary for submerged operation. In practice this is accomplished easily by stretching appropriately-sized surgical tubing over the end of the transducer. The option of providing a permanently-attached cable was rejected to simplify construction, to provide the user with greater operational flexibility, and to allow the rf connector to also provide atmospheric venting of the transducer during storage and shipping.

Although special-purpose units with other fundamental frequencies will be made available as needed, the general-purpose standard source intended to fit most applications will have a nominal fundamental resonance at 0.5 MHz. This choice allows odd overtone operation at output frequencies spaced 1 MHz apart, so that one transducer can suffice in many applications involving wide-band calibrations. Constraints on connecting cable size and breakdown voltage, and on size and complexity of the accompanying matching network dictate the use of a transducer element material of higher coupling constant than that of quartz. (In the present geometrical configuration, quartz elements of fundamental resonance below 2 MHz require impractically large drive voltages at higher power levels of interest. Also, harmonics spaced 4 MHz or more apart limit the usefulness of overtone operation.) Lithium niobate in the 36 degree Y-cut was chosen for use in our new transducers since, at a given resonance frequency, a transducer using lithium niobate requires approximately 5% of the drive voltage needed to obtain the same ultrasonic output power from a quartz transducer element. Tests of five prototype transducers have confirmed this and other favorable expectations. Stability of the lithium niobate transducers, as indicated by measurements of radiation conductance, has so far been indistinguishable from that

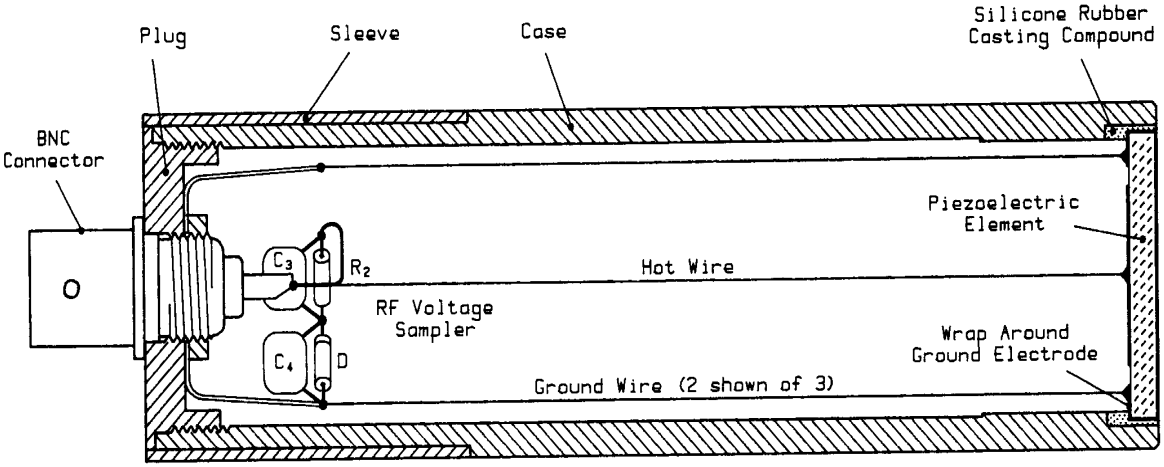

Figure 2—Longitudinal section of standard ultrasonic source.

of quartz transducers. Performance of the new transducers at overtone frequencies has been checked by both spot and swept-frequency tests. It has been found that good output is readily obtained at frequencies well above those needed by most users. Figure 3 shows the result of a swept-frequency measurement from 1 to 30 MHz. In this test, the error signal from the radiation force balance [3] was recorded while the transducer drive frequency was slowly increased; a crystal diode pickup connected at the transducer terminals was used to monitor input voltage to the transducer. Although this arrangement does not provide absolute measurements of output power [3], the test suffices to show that ample output can be obtained at high frequencies. The upper frequency limit for this experiment was determined by the test equipment. In other tests, similar output levels have been obtained at frequencies up to 78 MHz. Comparison of the data for transducer output power and transducer input power (as indicated by the square of the input voltage), has indicated that the decrease in output with increasing frequency cannot be attributed solely to decreasing drive voltage. Radiation force balance measurements of absolute power at spot frequencies up to 21 MHz have established that, despite the presence of additional loss mechanisms, at least one watt of indicated output can be obtained.

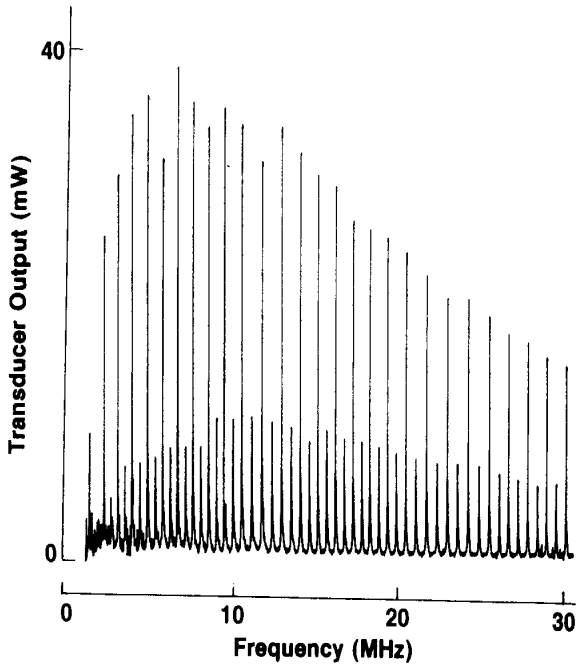

Figure 3 – Swept-frequency response of 0.5 MHz prototype transducer.

4. Conclusion

Design and operational details have been presented for a new system for ultrasonic power calibrations. Improvements over earlier versions include the mechanical design of the transducer and the provision inside each transducer of circuitry for measuring the applied voltage. This feature fosters improved accuracy by eliminating a radio-frequency measurement of voltage (replacing it with a dc measurement) and by reducing the number of computations needed for the overall procedure. Both the ease of use and the range of power levels attainable are increased by the availability in the new system of an impedance matching network of customized design. The use of a different material, lithium niobate, for the piezoelectric elements allows lower losses in the driving electronics, and more importantly, allows a lower fundamental resonance (0.5 MHz) than was previously used. This in turn allows overtone operation at convenient 1 MHz intervals. Because of its capability of multifrequency operation at such closely-spaced frequencies, the new transducer is "universal" in that one unit can replace several older units, each suitable only for single-frequency operation.

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